An Interstitial-Electron Model for the Structure of Metals and Alloys. V. Metal Alloys and Intermetallic Compounds

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(Received September 17, 1971)

On the basis of the interstitial-electron model for metals the essential feature of the metallic state is the relatively free movement of electrons, ($\bar{e}$), between interstices in a close-packed array of metal ions (positive cores). For a solid solution of one metal in another in which the metal ions have nearly the same size and core charge, the interstitial-electron structures which incorporate spatial and spin correlation of electrons are the same as for metals. Metallic properties can also result when the ratios of two less similar metals in an alloy are such as to give interstices with a constant ratio of the two metals surrounding them. Occupancy of such "homogeneous interstices" is the basis for intermetallic compounds and accounts for the Hume-Rothery rules. Intermetallic compounds such as γ phases (*e.g.* Cu_5Zn_8) are unique in that $\bar{e}$ and electron pairs must be assigned to two or more types of interstices which have different ratios of the two metal ions around them. This localization of $\bar{e}$ density explains the very poor conductivity, the hardness, the brittleness and the large diamagnetic susceptibility of γ phases. The structural framework of the interstitial-electron description accounts for the large composition range of the interstitial phases and can naturally include effects of ion core size and charge. Interpenetration of d^{10} ion cores by itinerant electrons which gives a balancing of the positive fields of the 2 ion cores accounts for the preponderance of d^{10} metals among intermetallic phases.

Of the metals, only Manganese has ions of two different core charges (and sizes), and Mn has unusual properties for a metal. However, with metal alloys there are always two or more ions of different size or core charge to be accomodated into the metallic structure. Where there are not large differences in effective positive fields of the metal ions making up the alloy the disruption of the periodic field will not be great enough to lead to large changes in properties. This situation holds for a great many alloys of similar metals. When the differences in positive field are very large, metallic salts or alloy salts[1] are formed. Some examples are Li_3B, Mg_3Sb_2, and Mg_2Sn. They have a metallic appearance but have unusually high melting points, are brittle and are very poor conductors of electricity. The alloy salt CsAu has been given[1] the structure Cs^+Au^-.

Between these two extremes of alloys, the solid solutions of one metal in another and the metallic salts, there are a large number of intermediate alloys which are called secondary alloys or intermetallic compounds. They are clearly metal-like but may deviate from metals in some property *e.g.* the intermetallic compound may be less ductile, it may be harder or brittle, or it may be a poor conductor.

There are a large number of different types of intermetallic compounds. The best known of these are the ones classified by Hume-Rothery[2] on the basis of the number of electrons per atom in the compound (or intermetallic phase). This ratio is 3/2 for β phases, 21/13 for γ phases and 7/4 for ε phases. All three types of intermetallic compounds form over rather wide composition ranges so the ratios are only approximate. In addition it has to be assumed that group VIII metals contributed no electrons in order to fit them into the ratio pattern.

Recent reviews[3-5] show the highly complex behavior and interrelations of α, β, γ, μ, and ε phases including both size effects and electronic effects.

The relations between the electronic structures of intermetallic compounds and that of metals, as well as the inter-relation between the various phases still remains obscure. Since the intermetallic compounds all form close-packed or nearly close-packed structures, it is anticipated that the interstitial-electron model[6] of metal structure can be applied to understanding the binding in intermetallic compounds as well as in metals. The term electron in an interstice refers to electron density considered to be localized in the interstitial binding region of the close-packed metal structure.[6]

Interstices in Intermetallic Compounds

It is proposed that a stable metallic structure can result for intermetallic compounds if the ratio of the two metal ions around an interstice is the same throughout the structure. This homogeneity of interstices can lead to the same free movement of electrons through the intermetallic structure as is observed for the metals themselves. The observed deviations from stoichiometry are understandable since a given structure can accomodate some deviation from homogeneity of interstices just as is the case for the solid solutions.

With this postulated basis for the formation of intermetallic compounds the structures for the various types of intermetallic phases can be considered and formulated using the Interstitial Electron Model.

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1) R. G. Nyholm, Proc. Tihany Symposium on Coordination Chemistry, Tihany, Hungary, 1965.

2) W. Hume-Rothery, *J. Inst. Metals*, **35**, 295 (1926).

3) M. V. Nevitt, "Electronic Structure and Alloy Chemistry of Transition Elements," ed. by P. A. Beck, Intersciences, New York (1963).

4) T. B. Massalski and H. W. King, *Prog. Materials Sci.*, **10**, 5 (1961).

5) J. M. Sivertson and M. E. Nicholson, *ibid.*, **9**, 305 (1961).

6) O. Johnson, This Bulletin, **45**, 1599, 1607 (1972).

β Phases

A typical example of a β phase occurs with a 50–50 Cu–Zn alloy which is known as β-brass. Other examples are Cu_3Ga, AlFe, and Cu_5Sn. They have Body-Centered Cubic (BCC) structures and ordinarily form a random structure of the two metals (β-form); tempering converts them to an ordered structure known as a "superlattice" (β′-form). For CuZn each ion forms its own simple cubic lattice. For Cu_3Al a double unit must be taken, and no superlattice has been observed for Cu_5Sn.

In formulating an electronic structure for the BCC β-phases based on the interstitial-electron model, the first question is which interstices are most likely to be occupied. Unsymmetrical oct interstices are chosen as most likely to be occupied by electrons in an unsymmetrical structure with two different metal ion cores. The relatively poor conductivity compared to pure metals and the low ductility of β-phases also makes it unlikely that tet rings of interstices are occupied by $\bar{e}$.

For CuZn (β-brass) the ion cores Cu^+ and Zn^{2+} give up 3 itinerant electrons to the BCC lattice of the intermetallic compound. The two unsymmetrical oct interstices can be designated as (Cu_2Zn_4) and (Cu_4Zn_2). A preference for electron occupancy of (Cu_2Zn_4) interstices is expected because of the stronger positive field exerted by Zn^{2+} as compared to Cu^+. There are 2 such interstices per unit cell of CuZn, and there can be occupancy of all 3 by $\bar{e}$. The geometry of interstices is discussed in detail in Part I.[6]

In such an arrangement of electrons, the $\bar{e}$ are separated widely enough to have random spins (see Part I).[6] Thus, the proposed low occupancy by $\bar{e}$ would give low paramagnetic susceptibility for the itinerant electrons and is in keeping with the diamagnetism of the β-phases. As far as the structure as a whole is concerned there is a network of adjoining homogeneous interstices, in this case the (Cu_2Zn_4), through which electrons can move as in other metallic structures.

The model characterizes β-phases as having occupancy of one of the two types of oct interstices which gives an electron/atom ratio of 3/2. The 3 interstices of one type can accomodate as few as 1 $\bar{e}$ or with electron pairing as many as 6 electrons per unit cell. This would give e/a ratios of 1/2 to 3 with the major number expected at 3/2 which is occupancy by $\bar{e}$ of one type of the oct interstices in BCC and presumably the occupancy with optimum binding energy for a metal. The 3/2 ratio is found for CuZn, Cu_3Al, Cu_5Zn, PdCu and related compounds. It is 5/2 for AlCo, FeAl, NiAl, NiGa, and NiIn and 6/2 for TiFe, VFe, and AlNd.

Some β-phases are ferromagnetic and offer an additional test for the model. There are also intermetallic compounds containing Fe, Co, or Ni which are not ferromagnetic. The compound NiAl is one such example. According to the interstitial-electron model the electronic structure for NiAl would be $|Al^{3+}, Ni^{10+}(d^8), 5e_{oct}|_{BCC}$. If the Ni ion cores occupy body center positions, electron occupancy will be of the (Ni_2Al_4) interstices on faces of the unit cell. The d-orbital axis of the $Ni^{10+}(d^8)$ core will be at 45° to the lattice axis because this directs d-orbitals toward Al^{3+} and not to itinerant electrons. The degeneracy of d-orbitals will be:

$\overline{xy}$ (to $\bar{e}_2$ on faces)

$\overline{z^2}$ (to $\bar{e}$ on faces)

$\overline{x^2-y^2}$ (to edges)

$\overline{xz}$ $\overline{yz}$ (toward Al)

This leads to complete pairing of d-electrons so no magnetic moment is expected on the Ni ion core. Electron occupancy of the (Ni_2Al_4) interstices by $5\bar{e}$ requires $2(\bar{e})_2$ and $\bar{e}$ per unit cell. This high ratio of $\bar{e}_2/\bar{e}$ is in keeping with the +Hall Coefficient observed for NiAl. For FeAl the structure $|Fe^{8+}(d^6), Al^{3+}, \bar{e}, 2(\bar{e}_2)_{oct}|_{BCC}$ is proposed and leads to all paired d-electrons for Fe iron cores as corner atoms in the unit cell and $\bar{e}$ and $(\bar{e})_2$ on faces. This is in agreement with the observed paramagnetism of FeAl. The magnetic properties of the compound CoAl have not been reported. The structure expected from the interstitial-electron model is $|Co^{9+}(d^7), Al^{3+}, \bar{e}, 2(\bar{e}_2)_{oct}|_{BCC}$, and the same degeneracy of d-orbitals to the NiAl and FeAl leads to 1 unpaired electron in an orbital toward a face. This alligns with an itinerant electron so this alloy is expected to be ferromagnetic. A $Co^{9+}(d^6)$ ion core would lead to no magnetic moment on cobalt. The background for this method of interpreting magnetic properties is given in Part IV.[7]

Magnetic properties are known for the series TiFe, VFe, and CrFe. Both TiFe and VFe form ordered β-phases. TiFe is not ferromagnetic while VFe has a saturation moment of 0.80 μ_B localized on Fe. Cr does not form a β-phase but is related and will be considered as having similar oct interstices; it has a saturation magnetization of 1.8 μ_B per iron atom. The interstitial-electron structure proposed for TiFe has a high d-localization which is necessary to limit the number of itinerant electrons to 6 which appeared to be the maximum observed for β-phases.

$$\left|Ti^{4+}, Fe^{8+}(d^6), 3(\bar{e}_2)_{oct}\right| BCC$$

When Fe ion cores are at body-centered positions the electron pairs are expected to be on face oct interstices (Ti_4Fe_2). The degeneracy expected is

$\overline{z^2}$ $\overline{xy}$ (to $2\bar{e}$ on faces)

$\overline{x^2-y^2}$ (to $\bar{e}$ on edge)

$\overline{xz}$ $\overline{yz}$ (to Ti).

There is no magnetic moment associated with this structure, in agreement with experimental data.

For VFe there must be still greater localization of d-electrons to keep within the maximum of 6 itinerant electrons. Thus an ion core $Fe^{8+}(d^7)$ is proposed for VFe.

7) O. Johnson, This Bulletin, **46**, 1923 (1973).

$$\left|V^{5+},\ Fe^{8+}(d^7),\ 3(\bar{e}_2)_{oct}\right|_{BCC}$$

This degeneracy of d-orbitals is the same as for TiFe, and with 7 d-electrons there will be one unpaired electron on the iron core. This is close to the observed magnetic moment for VFe. The increase in lattice contraction[3] from VFe to TiFe is probably due to the removal of some screening of the Fe ion core in going from 7 to 6 d-electrons (core charge from Fe^+ to Fe^{2+}).

The following structure is proposed for FeCr assuming it has the same occupancy of interstices as the β-phases:

$$\left|Fe^{8+}(d^6),\ Cr^{6+}(d^4),\ (\bar{e}_2),\ 2\bar{e}\right|_{oct}$$

Using the model, the unsymmetrical distribution of $\bar{e}$ and $(\bar{e})_2$ leads to 2 unpaired electrons on Fe and paired electrons on Cr. The data of Shull and Wilkenson[8] show a moment of 2 μ_B on Fe and no moment on Cr for the 50% alloy of Cr and Fe. The proposed structure for FeCr has fewer itinerant electrons (lower total ion core charges) than TiFe or VFe and weaker binding is expected. This agrees with the absence of lattice contraction[3] in FeCr.

There is a preponderence of intermetallic phases containing metal ion cores with d-electrons (*e.g.* Cu, Ag, Zn, Cd, *etc.*). This has been discussed by Nevitt[3] for β-phases. He suggests a special affinity for β-phase formation by the combination Group IV (*e.g.* Ti) and the Fe group and by Sc and the Cu, Zn group. There are two differences in the ion cores which contain d-electrons which may be responsible for stability of intermetallic phases with d-shell metals. One is the presence of d-electrons which can add to the binding strength. These d-electrons will be directed spatially in regions not occupied by interstitial electrons. The other difference is that d-shells are more easily deformed by positive fields of other ion cores and are more penetrable by itinerant electrons. This makes it possible for them to adapt to structures with another metal ion core and give greater homogeneity of interstices.

β-Manganese Phases

The β-Manganese type of compound has the same electron/atom concentration as the β-phases just discussed and will be included here for comparison. The crystal structure of β-Mn phases is a complex cubic type (tetragonal) with 20 atoms per unit cell. There are relatively few intermetallic compounds of this type which are also referred to as μ-phases.[4] These phases do not form superlattices. The interstitial-electron structures are given in Table 1.

Examination of the β-Mn structure indicates that interstices are approximately as in a face-centered cubic lattice, *i.e.* an oct edge interstice surrounded by 4 face and 2 corner ion cores and a central oct interstice surrounded by 6 face-centered ion cores. This is the basis for the interstices given in Table 1 and occupancy of a preferred 3/4 of the oct interstices (and the equivalent number of tet interstices) is the key to the 3/2 electron to atom ratio.

The interstitial-electron structure for Cu_5Si has three types of interstices. The stoichiometry requires that there is a 2/1 ratio of Cu/Si as corner atoms in the CCP scheme applied to interstices. In this case it is assumed that occupancy of 2 types of oct interstices is preferred to $\bar{e}$ pairing in tet. This provides an explanation for the difference in composition[4] for Cu_5Si as compared to Ag_3Al and $CoZn_3$.

It appears that $CoZn_3$ fits into the series by having additional $\bar{e}$ in tet interstices when the homogeneous oct interstices are occupied. The interstitial-electron structure proposed for $CoZn_3$ is

$$\left|Co^{9+}(d^7),\ 3Zn^{2+},\ 3\bar{e}_{oct},\ 3\bar{e},\ \bar{e}_{2tet}\right|_{\beta\text{-Mn}}$$

The degeneracy of d-orbitals for a corner cobalt ion core is as follows (where d-orbital axes are in coincidence with lattice axes):

$$\underset{z^2}{\uparrow} \qquad \underset{x^2-y^2}{\overline{}} \qquad \text{(to edges, } \bar{e} \text{ in oct)}$$

$$\underset{xy}{\uparrow\downarrow} \qquad \underset{xz}{\uparrow\downarrow} \qquad \underset{yz}{\uparrow\downarrow} \qquad \text{(to Zn)}$$

This gives a magnetic moment on Co of 1 unpaired $\bar{e}$ which is directed to oct $\bar{e}$. This makes the additional $\bar{e}$ in tet interstices a reasonable structure for balancing $\bar{e}$ distribution. The $CoZn_3$ (β-Mn phase) has been observed to be ferromagnetic by Koster and Schmidt.[9] The structure for $CoZn_3$ is a further demonstration of the limited nature of the electron concentration/atom approach which requires Group VIII metals to be zero valent to fit the ratios.

The structure for β-Mn was given in Part IV[7] as $|8Mn^{3+}, 12Mn^{+}, 36e|\beta$-Mn. This fits the present scheme with 15 $\bar{e}$ in oct interstices, 15 $\bar{e}$ and 3 $\bar{e}_2$ in tet interstices. This fits the paramagnetism observed (assume the d^4 and d^6 ion cores have d-electrons paired), and the

Table 1. Interstitial-electron structures for β-manganses phases[a]

Intermetallic compound	Composition range electrons/atom	Oct interstices	Tet interstices	Electron/atom ratio
Ag_3Al,[b] $(Ag_3^+Al^{3+})$	~1.4	$3(Ag_4Al_2)$, $1(Ag_2)$ $3\bar{e}\uparrow$	$8(Ag_3Al)$ $3\bar{e}\downarrow$	3/2
$2Cu_5Si$, $2(Cu_5^+Si^{4+})$	~1.5	$6(Cu_4Si_2)$, $3(Cu_5Si)$, $3(Cu_6)$ $6\bar{e}\uparrow$ $3\bar{e}\uparrow$	$16(Cu_3Si)$, $8(Cu_4)$ $9\bar{e}\downarrow$	3/2
$CoZn_3$, $(Co^{2+}Zn^{2+})$	~1.4	$3(Co_2Zn_4)$, $1(Zn_6)$ $3\bar{e}\uparrow$	$8(CoZn_3)$ $3\bar{e}\downarrow$, $\bar{e}_2$	2

a) See text concerning interstices occupied. b) Also Au_3Al.

8) C.G. Shull and M.K. Wilkenson, *Phys. Rev.*, **97**, 304 (1955).

9) W. Koster and H. Schmidt, *Z. Metallk.*, **46**, 468 (1955).

localization of e_2 in tet accounts for the brittleness and hardness.

ε-Phases

The ε-phase for brass occurs at approximately 75 atomic % zinc, and the structure is written $CuZn_3$. ε-Phases have hexagonal close packing (HCP) with less than the normal ratio for c/a, and the metal ion cores are randomly arranged in HCP ε-phases. The lattice distortion of HCP gives the structure 4 oct and 4 bipyramidal interstices[6] per 4 ion cores ($CuZn_3$). For bipyr interstices to be completely occupied there must be only 1/2 occupancy of oct interstices because of the specific electron spin restrictions of the distorted HCP (see Part I).[6] The other restrictions on interstice occupancy, *e.g.* for $CuZn_3$, are (1) there is preferential occupancy of $CuZn_5$ oct interstices over $CuZn_4$ oct due to the difference in fields of the ion cores. (2) There is preferential occupancy of $CuZn_4$ bipyr over Cu_2Zn_3 bipyr which are in ratio of 3 $CuZn_4$ to 1 Cu_2Zn_3. In placing itinerant electrons in the interstices the maximum of 3 $\bar{e}$ are placed in $CuZn_4$ bipyr and the remaining 4 as $\bar{e}$ and $\bar{e}_2$ in $CuZn_5$ oct and $\bar{e}$ in $CuZn_4$. Thus, the electronic structure for $CuZn_3$, a typical example of the β-phase is:

$$\left|Cu^+, 3Zn^{2+}, \bar{e}_2, 2\bar{e}_{oct}, 3\bar{e}_{bipyr}\right|_{HCP}$$

The unique requirements of the distorted HCP lattice explains the 7/4 e/a ratio of Hume-Rothery for most of the ε-phases, and the greater electron density in oct interstices is as expected for distortion of the HCP lattice in the non-axial direction (see Part II).[6] See Table 2.

Table 2. Interstitial-electron structures for ε-phases

Intermetallic compound	Electron/atom conc. range	Fractional occupancy of interstices		Electron/atom ratio
		bipyr.	Oct	
$CuZn_3$[a)]	1.78—1.85	3/4	$1/2\bar{e}$, $1/4\bar{e}_2$	7/4
Cu_3Sn[b)]	1.75	3/4	$1/2\bar{e}$, $1/4\bar{e}_2$	7/4
Ag_5Al_3[c)]	1.54—1.86	3/4	$1/2\bar{e}$, $1/4\bar{e}_2$	7/4
$FeZn_7$	—	$5/8(\bar{e}_2)$	$3/4\bar{e}$	8/4
Sb_3Cu_{13}[d)]	—	3/4	$1/2\bar{e}$, $1/4\bar{e}_2$	7/4

a) Also $CuBe_3$, $CuCd_3$, $AgZn_3$, $AgCd_3$, $AuZn_3$, $AuCd_3$.
b) Also Cu_3Ge, Ag_3Sn, Au_3Sn, Cu_3Si.
c) Also Au_5Al_3.
d) Also Sb_3Ag_{10}.

The interstitial-electron structure proposed for FeZn is (where bp=bipyramidal interstice)

$$\left|Fe^{8+}(d^6), 7Zn^{2+}, 6\bar{e}_{oct}, (5\bar{e}_2)_{bp}\right|_{HCP}$$

This stoichiometry $FeZn_7$ gives a ratio of $5(FeZn_4)$ and $3(Zn_5)$ bp interstices and a ratio of $6(FeZn_5)$ and $2(Zn_6)$ oct interstices. To place 16 $\bar{e}$ in conformity with lattice restrictions requires 5 $\bar{e}_2$ in B.P. and 6 $\bar{e}$ in oct. The degeneracy of d-orbitals on Fe in $FeZn_7$ is expected to be the same as for Ru metal in HCP (see Part IV),[7] and the six d-electrons are all paired. The Ag_5Al_3 ε-phase has a still different pattern of interstices, and Massalski[4] has not included it with the ideal ε-phases. A possible electron structure is

$$\left|5Ag^+, 3Al^{3+}, 2(\bar{e}_2), 4\bar{e}_{oct}, 6\bar{e}_{bipyr}\right|_{HCP}$$

Here the bp interstices are in a ratio of $7Ag_3Al_2$ to one Ag_4Al and the oct interstice $6Ag_4Al_2$ to $1Ag_3Al_3$. A greater range of composition is expected since one more $\bar{e}$ can be accommodated in bp interstices. The Cu_3Sn phase fits the scheme for the other ε-phases if Cu is taken to have the stronger field in influencing preference within the bipyr interstices. This may be the case since the work function for Cu (4.4) is greater than that of Sn (4.2 eV).

None of the pairs of occupied interstices in ε-phases can be considered to be homogeneous, and there is relatively large localization of $\bar{e}$ in certain interstices proposed in the above structure so the movement of electrons from the occupied to vacant interstices will be more difficult than in pure metals. This restriction of electrons is reflected in the greater hardness and brittleness and relatively low electrical conductivity of ε-phases as compared to β-phases.

γ-Phases

As seen in Table 3 the compositions of γ-phases are rather complicated. These intermetallic compounds are exceptionally hard and brittle, and they have low electrical conductivity. They show a pronounced maximum in diamagnetic susceptibility over the small increases shown *e.g.* for brass by the β and ε phases.

A neutron diffraction study[10] has confirmed the structure of Cu_5Cd_8 and Cu_9Al_4, and the authors discussed the arrangement of ions in terms of inner and outer tetrahedral and octahedral positions in agreement with recent X-ray data[11] indicating a close-packed structure. The symmetry of Cu_9Al_4 is slightly different than that of the two other intermetallic phases. The γ-phase structure can also be discussed in terms of the small BCC units, and as in β-phases it is assumed that $\bar{e}$ will occupy the unsymmetrical octahedral interstices of these individual BCC unit cells. This can be done in a straight-forward manner even for these complex lattices if the true unit cell of 52 ions is broken up into individual AB unit cells with corner and body center ions assigned so as to give the correct over all composition.

For Cu_5Zn_8 (unit cell is $Cu_{20}Zn_{32}$) the structure can be divided into the following groups of BCC unit cells:

$$\left|8(Cu_7Zn_1, Zn_8), 1(Cu_5Zn_3, Zn_8), 1/2(Cu_2Zn_2, Zn_4)\right|$$

where for each group the first two atoms listed are the corner atoms and the last one the body center atoms. All of the face oct and edge oct interstices in these units can be listed and when grouped together they are:

face oct; $\underline{18(Cu_2Zn_4)}$, $24(Cu_4Zn_2)$ and $36(Cu_3Zn_3)$ total=78
edge oct; $\underline{42(Cu_2Zn_4)}$ and $36(CuZn_5)$ total=78

10) O. Heidenstam, A. Johansson, and S. Westman, *Acta Chem. Scand.*, **22**, 653 (1968).
11) W. B. Pearson, J. K. Brandon, R. K. McMillan, and R. Brizzard, *Acta Crystallogr.*, **A28**, 596 (1972).

TABLE 3. ELECTRONIC STRUCTURE OF γ-PHASES[e]

Compound	Unit cell groups	Face oct	Edge oct	Interstice occupancy[f]	
Cu_5Zn_8[a]	$8(Cu_7Zn_1, Zn_8)$	$\underline{18Cu_2Zn_4}$	$\underline{42Cu_2Zn_4}$	$18\bar{e}\uparrow$	$18\bar{e}\downarrow$
$(Cu_{20}Zn_{32})$	$1(Cu_5Zn_3, Zn_8)$	$24Cu_4Zn_2$	$36CuZn_5$		$24(\bar{e})_2$
	$1/4(Cu_4Zn_4, Zn_8)$	$36Cu_3Zn_3$			
Cu_9Al_4[b]	$3(Cu_3Al_5, Cu_8)$	$\underline{42Cu_4Al_2}$	$\underline{18Cu_4Al_2}$	$18\bar{e}\uparrow$	$18\bar{e}\downarrow$
$(Cu_{36}Al_{16})$	$1/4(Cu_4Al_4, Cu_8)$	$36Cu_3Al_3$	$60Cu_5Al$	$24(\bar{e})_2$	
$Li_{10}Pb_5$	$2(Li_5Pb_3, Li_8)$	$\underline{42Li_4Pb_2}$	$\underline{18Li_5Pb_2}$	$18\uparrow$	$18\downarrow$
$(Li_{40}Pb_{12})$	$1(Li_5Pb_3, Li_8)$	$24Li_5Pb$	$42Li_5Pb$	$24(\bar{e})_2$	$(4\bar{e}?)$
	$1/4(Li_4Pb_4, Li_8)$	$12Li_3Pb_3$	$18Li_6$		
$Cu_{31}Sn_8$[c]	$4(Cu_5Sn_3, Cu_8)$	$63Cu_4Sn_2$	$\underline{24Cu_4Sn_2}$	$24\uparrow$	$24\downarrow$
$(Cu_{62}Sn_{16})$	$3/8(Cu_4Sn_4, Cu_8)$	$48Cu_5Sn_1$	$42Cu_5Sn$	$39\bar{e}_2$	
	$1/2(Cu_3Sn_5, Cu_8)$	$6Cu_3Sn_3$	$3Cu_4$		
$Li_{10}Ag_3$	Assume 1/3 occupancy of oct interstices			$26\uparrow$	$26\downarrow$
$(Li_{40}Ag_{12})$					
Fe_5Zn_{21}[d]	$1(Zn_6Fe_2, Zn_8)$	$84Fe_2Zn_4$	$\underline{120FeZn_5}$		$48\bar{e}_2$
$(Fe_{20}Zn_{84})$	$4(Zn_5Fe_3, Zn_8)$	$\underline{72FeZn_5}$	$36Zn_6$	$72\bar{e}\uparrow$	$72\bar{e}\downarrow$
	$1\ 1/2(Zn_4Fe_4, Zn_8)$				

a) Also Cu_5Cd_8, Ag_5Zn_8, Ag_5Cd_8, Au_5Zn_8, Au_5Cd_8, and Au_5Hg_8.
b) Also Cu_9Ga_4, Cu_9In_4, and Ag_9Al_4.
c) Also $Ag_{31}Sn_8$ and $Na_{31}Pb_8$ (unit of $Cu_{62}Sn_{16}$ has 117 unit cells, 128 $\bar{e}$)
d) Also Ni_5Zn_{21}, Rh_5Zn_{21}, Pd_5Zn_{21}, Pt_5Zn_{21}, and Ni_5Cd_{21}. (Ternary systems are $Cu_7Zn_4Al_2$, Cu_6Zn_6Al, and $Cu_2Al_3Zn_2$.)
e) Underlined interstices assumed to be occupied by electrons.
f) Most frequent e/a ratio is 21/13. The exceptions are $Li_{10}Ag_{13}$ (13/13), $Li_{10}Pb_3$ (22/13) and Fe_5Zn_{21} (26/13).

The criteria for deciding electron occupancy will be (1) the greatest homogeneity of interstices, (2) the maximum field of ions and (3) the balancing of electron spins. These preferred interstices are underlined above and in Table 3. The following distribution of electrons places the maximum number of $\bar{e}$ in these two interstices with the additional interstices occupied by electron pairs (there is complete occupancy of the preferred interstices):

$\underline{18Cu_2Zn_4}$ (face oct), $18\bar{e}$ $\underline{42Cu_2Zn_4}$ (edge oct), $18\bar{e}$, $24(\bar{e})_2$

This assignment of the 84 $\bar{e}$ of $Cu_{20}^{+}Zn_{32}^{2+}$ gives a structural explanation of the 84/52 or 21/13 Hume-Rothery ratio for γ-phases. The localization of $\bar{e}$ in certain interstices and presence of a large number of electron pairs is in keeping with the extreme hardness and brittleness and the low electrical conductivity of γ-phases as well as their high diamagnetic susceptibility (reduction in paramagnetic susceptibility). (An alternate placement of $\bar{e}$ as 24 $\bar{e}$ in Cu_4Zn_2, 18 $\bar{e}$ in Cu_2Zn_4 face oct and 42 $\bar{e}$ in Cu_2Zn_4 edge oct is also a possibility but would not account for the unusual properties.)

Table 3 lists some other γ-phases and lists the interstices in the same way as illustrated above for Cu_5Zn_8. The interstice pattern accounts for the electron/atom ratio is all of the cases except $Li_{10}Ag_3$. Here it is considered that this compound is an exception due to the weak forces of the two metal ion cores. It has an electron to atom ratio of 13/13. A 1/3 occupancy of edge and face oct can explain the electron/atom ratio. It would appear that the similarity to other γ-phases is coincidental for $Li_{10}Ag_3$.

The structure for $Li_{10}Pb_3$ suggests similarity to other γ-phases, but the Hume-Rothery e/a ratio is 22/13. The structure given in Table 4 requires placement of 4 additional electrons (out of 88). It may be that the stoichiometry $Li_{10}Pb_3$ is not exact, or it may be that the large difference in ion cores leads to occupancy of more than one type of interstice.

The compound Fe_5Zn_{21} is also included in the same interstice scheme as the majority of γ-phases with an ion core of $Fe^{8+}(d^4)$. This leads to no unpaired electrons on the iron since the degeneracy of d-orbitals is the same as for β-phases. As given in Table 3 the preferred interstices for Fe_5Zn_{21}, are 8 $\bar{e}$ (out of 248) short of being completely occupied. This can reflect the extension of $\bar{e}$ in d-orbitals into interstices and a small stoichiometry change would be indicated. Another possibility is that interstices surrounded only by Zn are preferred by itinerant electrons because of absence of d-electrons directed into these interstices.

The small Hall Coefficient[4] for γ-phases can be explained by the presence of both $\bar{e}_2$ and vacancies in the structure. In cases like this electric current can be carried both by dissociation of $\bar{e}_2$ and by $\bar{e}$ movement through interstices. The strong interstice preference in γ-phases with resultant presence of many $(\bar{e})_2$ leads to a polarity in the structure; regions of vacant interstices have a net positive charge and regions with $(e)_2$ a net negative charge.

Laves Phases

A special group of intermetallic compounds which is composed of metal ions of different sizes and which have more exact compositions than the intermetallic phases considered above are the Laves phases. These compounds are all close-packed structures and include both binary (AB_2) and ternary (A, BC) compounds. As an example of structure, $MgCu_2$ has cubic close packing, and the two metal ions form two interpenetrating lattices; Mg^{2+} is surrounded by 12 Cu^{+} and Cu^{+} by 6 Mg^{2+}. A few Laves phases are listed in Table 4 with proposed interstitial electron structure.

TABLE 4. INTERSTITIAL-ELECTRON STRUCTURES FOR LAVES PHASES

	Compound (AB_2)	Occupancy of interstices[b]		
		Tetrahedral		Octahedral
		($4AB_3$)	($2A_2B_2$)	$3(A_2B_4)$
Type 1 (CCP)	$MgCu_2$	—	$2\bar{e}\uparrow$	$2\bar{e}\downarrow$
	$AgBe_2$	$2\ 1/2\bar{e}\uparrow$	—	$2\ 1/2\bar{e}\downarrow$
	$NaAu_2$	—	$1\ 1/2\bar{e}\uparrow$	$1\ 1/2\bar{e}\downarrow$
	Mg(NiZn)	$3\bar{e}\uparrow$	—	$3\bar{e}\downarrow$
	KBi_2	$\uparrow 3\bar{e}, 1/2\bar{e}_2$	—	$3\bar{e}\downarrow$
	ZrW_2	$\uparrow 3\bar{e}$	—	$3\bar{e}\downarrow$
	$ZrZn_2$[a]	$\uparrow 3\bar{e}$, $(\bar{e})_2$ or $(\bar{e})$?		$3\bar{e}\downarrow$
Type 2 (HCP)	$MgZn_2$	$3\bar{e}\uparrow$	—	$3\bar{e}\downarrow$
	$CaMg_2$	$3\bar{e}\uparrow$	—	$3\bar{e}\downarrow$
	Ca(AgAl)	$3\bar{e}\uparrow$	—	$3\bar{e}\downarrow$
	$TiFe_2$	$\uparrow 3\bar{e}, \bar{e}_2$	—	$3\bar{e}\downarrow$
Type 3	$MgNi_2$	$3\bar{e}\uparrow$	—	$3\bar{e}\downarrow$
	Mg(CuAl)	$3\bar{e}\uparrow$	—	$3\bar{e}\downarrow$
	$TiCo_2$	$\uparrow 3\bar{e}, \bar{e}_2$	—	$3\bar{e}\downarrow$
	$ScFe_2$	$\uparrow 3\bar{e}, 1/2\bar{e}_2$	—	$3\bar{e}\downarrow$
	$ThMg_2$	$\uparrow 3\bar{e}, \bar{e}_2$	—	$3\bar{e}\downarrow$
	$NbZn_2$	$\uparrow 3\bar{e}, 1/2\bar{e}_2$	—	$3\bar{e}\downarrow$

a) Ferromagnetic Laves Phase (S. J. Pickart, H. A. Alperin, G. Shirane, and R. Nathans, *Phys. Rev. Lett.*, **12**, 444 (1964)).

b) Fractions used for a single unit cell.

Close-packed structures of the type AB_2 have octahedral interstices (A_2B_4 neighbors) which are all identical, but the tetrahedral interstices are of two types (AB_3 and A_2B_2 neighbors). It appears most likely that the electrons will occupy octahedral interstices and those tetrahedral interstices with highest + fields. When ion core A has the highest+field, the tet interstice A_2B_2 is occupied; when ion core B has the highest+ field, interstice AB_3 is occupied. This is done for the compounds in Table 4. These compounds cover a wide range of electron/atom ratios (given by Nevitt[3]). The compounds which have more electrons than the number which fill the preferred octahedral and tetrahedral interstices with single $\bar{e}$ are those with ions having unfilled d-shells. This is a classification pointed out by Raynor,[12] and these compounds also show considerable lattice contraction upon formation. The proposed structures for these latter compounds have $\bar{e}_2$ in tet interstices.

The Laves phase KBi_2 represents an exceptional compound. It has a melting point of 553°C, and there is a very large lattice contraction upon formation of KBi_2. Since Bi metal does not have a close-packed structure and may have electron pairs within the layer of bismuth ions[6] there may be a greater change in pattern of $\bar{e}$ in interstices of KBi_2 than in formation of other Laves phases. The structure as given in Table 4 assumes an ion core of Bi^{3+} for Bismuth and does have $\bar{e}_2$ in the tet interstice.

When a transition metal with localized d-electrons is present there is interaction between the $(\bar{e})$ of the interstices and the localized d-electrons. This could explain the non-existence of $TiNi_2$ whereas $TiFe_2$ and $TiCo_2$ both form. This probably comes about because the degeneracy of d-orbitals in the HCP lattice (see Part IV) directs d-electrons toward tet interstices for $Fe(d^6)$ and $Co(d^6)$ but to both oct and tet for $Ni(d^8)$.

The interstitial-model indicates that the key to the $\bar{e}$ distribution in Laves phases is the change in occupancy of A_2B_2 tet interstices as there is a change from B to A as the ion core with highest+field. Lattice contractions appear to be associated with $(\bar{e})_2$ in the structure. It is of interest that the Laves phase $ZrZn_2$ exhibits itinerant ferromagnetism. As indicated in Table 4 this could come about if an unpaired $\bar{e}$ went into the A_2B_2 tet interstice instead of $\bar{e}_2$ in AB_3. Pairing of $\bar{e}$ is observed for Laves phases with d-electrons localized on ion cores and for KBi_2, $ThMg_2$, and $NbZn_2$ and may not occur in the case of $ZrZn_2$.

Miscellaneous Alloy Phases

The Na–Pb System is of interest because there are maxima in the phase diagram, but $Na_{31}Pb_8$ (a γ-phase) appears to be the only definite intermetallic compound. The special stability for certain compositions can be accounted for on the basis of the interstitial-electron model in the following way. The Na–Pb system forms a CCP lattice ($AuCu_3$ structure) with Na in corner positions and with a small portion of the Pb face center ions replaced by Na. The ideal phase $NaPb_3$ would have 13 $\bar{e}$ to be distributed among 4 oct and 8 tet interstices and is not observed. The phase maximum at Na_2Pb_5 represents replacement of 1Pb out of 18 (5.5%) by Na. Such a structure of 7 ion cores would have 7 oct and 14 tet interstices (11 of which are homogeneous with oct). Occupancy of oct by $7\bar{e}(\uparrow)$ and tet by $7\bar{e}(\downarrow)$ and $4(\bar{e})_2$ gives complete occupancy of preferred interstices. Greater % of Na leads to insufficient $\bar{e}$ to occupy all preferred interstices for an $AuCu_3$ structure. It appears that there is a stability for Na_2Pb_5 based on interstice occupancy which is similar to other intermetallic phases, but the small fraction of (or random nature of) face-centered Pb replaced by Na is insufficient to lead to a definite compound.

Discussion

The Interstitial-Electron Model gives reasonable structures for the wide variety of alloy phases and accounts for the existence and stability of intermetallic phases in the following way. A combination of 2 or more metal ion cores can achieve stability and metallic properties when a given structure provides an appropriate number of homogeneous interstices for the number of itinerant electrons available. A given structure will have an optimum number of interstices and variations in this optimum are expected with variations in core charge and ion core size. In this way the model incorporates the Hume-Rothery *e/a* ratio as a special case, and makes it possible to include discussion of the effect of d-electrons, of lattice contraction and changes in many properties in the framework of a comprehensive model for metals and alloys.

12) G. V. Raynor, "Physical Chemistry of Metallic Solutions and Intermetallic Compounds, Symposium," Vol. 1, Chemical Publishing Co., New York (1960).

The focussing on electrons in interstices gives insight into the variation in properties of an intermetallic compound in cases where electron concentration or radius-ratio failed to account for changes in properties. An example given by Nowotny *et al.*[13] is $LaNi_2$, a Laves phase which shows a strong lattice contraction. Nowotny suggests the polarity of La^+Ni^- but points out that Pauling assumed the opposite polarity on the basis of his interatomic distance relationships. The polarity arising in the Interstitial-Electron Model requires neither of these extremes. As pointed out for γ-phases for structures with strong preference for $\bar{e}$ occupancy of certain interstices, there will be interstitial regions with net + charge and others of net − charge. Lattice contractions to compensate for this lead to more uniform charge distribution.

13) H. Nowotny, F. Holub, and A. Wittmann, *ibid.*, Vol. 1.