the total number of the atoms in all stages of ionization given by Menzel[5] with the distribution between stages given by Russell.[6] As in Table I, the transition probabilities, A, are taken from Pasternack[4] or are extrapolated from his values. The equivalent widths in the seventh column were calculated with the aid of formula (1). Since the measurement of equivalent widths smaller than 0.001A seems to be impractical with present techniques, it is evident that investigations are limited to three lines. The wave-lengths of two of these lines, λ7724.7 and λ8727.4, are not known at the present time with sufficient accuracy to make positive identifications in the solar spectrum possible. The third line, at λ10991.52, falls so close to an atmospheric line at λ10991.40 that equivalent-width measurements will at best be very uncertain.

In conclusion, the author wishes to express his indebtedness to Mr. H. D. Babcock and Dr. Leo Goldberg for many helpful discussions concerning problems of identification and of theory, to Dr. S. B. Nicholson for taking the solar spectrograms used in this investigation, and to Dr. P. W. Merrill for the use of the spectrograms of HD 45677.

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[6] H. N. Russell, Mt. W. Contribution No. 383; Ap. J. 70, 11 (1929).

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The Ratio of Valence Electrons to Atoms in Metals and Intermetallic Compounds*

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It is shown that the numbers of valence electrons assigned to the γ-alloys, β-manganese and alloys with similar structure, and α-manganese by a new system of metallic valences agree closely with the electron numbers calculated for complete filling of important Brillouin polyhedra for these structures.

I. INTRODUCTION

WHEREAS chemical valence theory has provided a satisfactory systematization of the formulas of most organic and inorganic compounds, the intermetallic compounds have continued to present a puzzling problem. Some intermetallic compounds, such as Mg_2Sn, have formulas that can be correlated with the customary valences of the elements involved. Many others, however, seem to show in their formulas no correlation with chemical valence: examples are $NaCd_2$, KHg_{13}, Cu_5Zn_8, $Cu_{31}Sn_8$, Cu_9Al_4, Fe_5Zn_{21}. Added interest is given to the problem by the fact that the last four of these compounds, with formulas that seem to show little relation to one another, are sufficiently similar in their properties, and different from other intermetallic compounds, to indicate that they are to be classified together.

Only in recent years has progress been made in attacking the problem presented by these intermetallic compounds; at the present time we may say that, although there are a number of puzzling questions that remain unanswered, the beginning of a theory of the stability and other properties of the substances has been formulated.

Let us first consider, as an example, the copper-zinc system of alloys.[1,**] The ordinary yellow brass of commerce is restricted in composition to the first (copper-rich) phase of the system. This phase, which has the face-centered cubic structure characteristic of copper, is followed successively, as the zinc content is increased, by the β-phase (body-centered cubic),

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** References are listed in the bibliography at the end of the paper.

γ-phase (with a complex cubic structure), ϵ-phase (close-packed hexagonal, with axial ratio c/a less than $(8/3)^{\frac{1}{2}}$), and the η-phase (close-packed hexagonal, with c/a greater than $(8/3)^{\frac{1}{2}}$, terminating in pure zinc). The α- and η-phases are regarded as primary solid solutions in the parent metals, but the intermediate phases have compositions that can be described approximately by relatively simple chemical formulas, CuZn for the β-phase, Cu_5Zn_8 for the γ-phase, and $CuZn_3$ for the ϵ-phase.

In other systems of binary alloys similar phases are found. The simple structure characteristic of the β-phase, with two atoms in a cubic unit cell, at positions 000 and 1/2 1/2 1/2, is shown by the compounds AgZn, AgCd, AuZn, AuCd, and CuBe. The compounds Cu_3Al and Cu_5Sn, with different formulas, also have structures related to the body-centered structure for pure metals. In 1926, even before complete x-ray investigations of these compounds had been published,[2] Hume-Rothery[3] suggested that the β-phases CuZn, Cu_3Al, and Cu_5Sn are analogous in structure. He further pointed out that if valences of 1, 2, 3, and 4 are assigned to metals of groups I, II, III, and IV of the periodic table, a constant ratio 3/2 of valence electrons to atoms is displayed by these β-phase compounds (CuSn, $(2+1)/2=3/2$; Cu_3Al, $(3+3)/4=3/2$; Cu_5Sn, $(5+4)/6=3/2$). This observation led him to conclude that certain metal structures are stabilized by the possession of a definite ratio of valence electrons to atoms, this ratio being equal to 3/2 in the case of the arrangement characteristic of the β-phase. In the course of the next few years this rule was extended by various investigators, chiefly Westgren and Phragmén[4] and Bradley and Thewlis.[5] They showed that in a large number of different alloy systems the β-, γ-, and ϵ-phases appear at or near electron-to-atom ratios of 3/2, 21/13, and 7/4, respectively, calculated with the usual valence values for the elements. In some systems they found, instead of the β-phase, a complex structure similar to β-manganese appearing at the ratio 3/2 (for example, Ag_3Al).

In order to bring β-phases such as FeAl and CoAl into correspondence with the rule it was necessary to assign the valence of zero to the transition elements manganese, iron, cobalt, and nickel and to their congeners, the palladium and platinum metals. In spite of this element of arbitrariness the Hume-Rothery rule has served to organize and to simplify a large amount of data relative to alloy systems.[6] The known examples of the Hume-Rothery phases and intermetallic compounds of similar structure, including the β-manganese structure, are listed in Table I. Not all of the compounds shown here have the electron-atom ratio demanded by the Hume-Rothery rule.

The γ-alloys are compounds with complex formulas, the cubic unit of structure containing 52 atoms or a multiple of 52 atoms. For these alloys the Hume-Rothery ratio is a constant at 21/13, with two exceptions, $Li_{10}Pb_3$ at 22/13 and $Li_{10}Ag_3$ at 13/13. The evidence is accordingly strong that the electron-atom ratio is important in stabilizing these structures. It seems likely that it is also important for β-manganese, with 20 atoms per unit cube, and also for the ϵ-structure. The β-phase structure, however is so simple, consisting of atoms placed at the points of a body-centered cubic lattice, that it might well be expected that factors other than the electron-atom ratio, such as the relative sizes of the atoms, would be determinative in the selection of this structure, and it is accordingly not surprising that nearly half of the β-phase intermetallic compounds listed in Table I show Hume-Rothery ratios different from 3/2.

The β- and ϵ-phases are not unlike their component metals in properties such as luster, malleability, and electrical resistivity. The γ-phase, however, shows striking differences: it is brittle and is associated with sharp maxima in electrical resistivity[7] and diamagnetic susceptibility.[8]

The theoretical significance of the Hume-Rothery rule and the quantum mechanical explanation of the curious properties of the γ-alloys have been discussed by Jones.[9] Jones' treatment is based upon the study of the effect of the periodic potential of a lattice in which electrons are moving in producing bands or zones of energy levels.[10, 11] It was found that the energy of the electron moving in a periodic field may be a discontinuous function of its momentum, and L. Brillouin[12] recognized that the points of discontinuity correspond to Bragg reflection of the electrons from crystallographic planes of the crystal. The geometrical conditions for this sort of perturbation can be described in a space which is at the same time momentum space for the electron and reciprocal-lattice space for the crystal; perturbations occur when the momentum vector terminates on polyhedral surfaces. We shall call these polyhedra Brillouin polyhedra and the zones of energy levels between the polyhedral surfaces Brillouin zones.[13] The Brillouin polyhedra can be described by assigning to the faces the crystallographic indices of the planes which by Bragg reflection of the electron produce the perturbation that concentrates the energy levels into zones.

Jones pointed out that the energy discontinuities produced in this way are large only for planes from which the electrons are reflected strongly; that is, for planes with a large structure factor for electrons. Usually these are also planes which give strong x-ray reflections, although in special cases, when the relative scattering powers of atoms of two elements for slow electrons are considerably different than for x-rays, this criterion may not be valid. Jones observed that the physical properties shown by the γ-alloys are those which would be expected for a metallic crystal with a completely filled or nearly completely filled Brillouin zone. He noted that the first two strong x-ray reflections shown by γ-brass, Cu_5Zn_8, those from the forms $\{330\}$ and $\{411\}$, determine a Brillouin polyhedron of volume $45/a_0^3$ (a_0 being the edge of the unit cube), which leads to occupancy by 90 electrons per unit cell of 52 atoms. The Hume-Rothery ratio of 21/13 corresponds to 84 electrons per 52 atoms; accordingly the zone is $84/90=93.5$ percent filled. This might be considered sufficient to explain the filled-zone properties of γ-brass, and it was indeed supposed by Jones that the number of electrons required to fill a zone is somewhat less than the volume of the Brillouin polyhedron. The argument for this, however, is not very clear, and, in particular, there is no reason to expect the stabilization to occur exactly at 84/52, in place of 90/52. In a similar treatment of alloys with the β-manganese structure, containing 20 atoms per cubic unit cell, Mott and Jones[9] found that there is a Brillouin polyhedron containing 32.4 electrons per unit cell of 20 atoms. Since the Hume-Rothery ratio is 3/2 this zone is $30/32.6=92$ percent filled. In the consideration of the β-phase alloys Mott and Jones[9] found that the first strong reflection from the body-centered cubic lattice, $\{110\}$, gives a Brillouin polyhedron (constituting the first Brillouin zone) that contains 4 electrons per atom, so that the Hume-Rothery ratio 3/2 represents only a partial (75 percent) filling. This is in agreement with the highly metallic character of this phase, the alloys being malleable and good conductors of electricity, and having normal magnetic properties. Mott and Jones pointed out that a sphere inscribed in the $\{110\}$ Brillouin polyhedron contains 1.480 electrons per atom, which is essentially equal to the customary Hume-Rothery ratio, and they suggested that, in this instance, stabilization occurs when the spherical surface of the momentum sphere first touches the Brillouin polyhedron; that is, at values of the momentum for which Bragg reflection first appears, in certain directions.

TABLE I. Hume-Rothery phase.

Phase	β		β-Mn		γ		ϵ	
Type in Strukturbericht	$B2$ and $L20$		$A13$		$D81, 82, 83, 84$			
Character	body-centered cubic		complex cubic		complex cubic		hexagonal close packed $c/a<(8/3)^{1/2}$	
Atoms per unit cell (minimum)	2		20		52		2	
	Compounds	H-R ratio	Compounds	H-R ratio	Compounds	H-R ratio	Compounds	H-R ratio
Compounds formed, with Hume-Rothery ratio electrons: atoms	CuZn	3/2	β-Manganese	0	Cu_5Zn_8	21/13	$CuZn_3$	7/4
	AgZn	3/2			Cu_5Cd_8	21/13	$CuBe_3$	7/4
	AgCd	3/2	Ag_3Al	3/2	Ag_5Zn_8	21/13	$CuCd_3$	7/4
	AuZn	3/2	Au_3Al	3/2	Ag_5Cd_8	21/13	$AgZn_3$	7/4
	AuCd	3/2	Cu_5Si	3/2	Au_5Zn_8	21/13	$AgCd_3$	7/4
	Cu_3Ga	3/2	$CoZn_3$	3/2	Au_5Cd_8	21/13	$AuZn_3$	7/4
	Cu_5Sn	3/2			Au_5Hg_8	21/13	Cu_3Sn	7/4
	BeCu	3/2			Cu_9Al_4	21/13	Cu_3Ge	7/4
	MgAg	3/2			Cu_9Ga_4	21/13	Ag_3Sn	7/4
	AlFe	3/2			Cu_9In_4	21/13	Au_3Sn	7/4
	AlCo	3/2			Ag_9Al_4	21/13	Au_5Al_3	7/4
	AlNi	3/2			$Cu_{31}Sn_8$	21/13	$FeZn_7$	7/4
	$AlCu_3$	3/2			$Ag_{31}Sn_8$	21/13		
	LiHg	3/2			Fe_5Zn_{21}	21/13		
	LiAg	1.0			Co_5Zn_{21}	21/13		
	LiTl	2.0			Ni_5Zn_{21}	21/13		
	BeCo	1.0			Rh_5Zn_{21}	21/13		
	BePd	1.0			Pd_5Zn_{21}	21/13		
	MgHg	2.0			Pt_5Zn_{21}	21/13		
	MgTl	2.5			Ni_5Cd_{21}	21/13		
	CaTl	2.5			$Cu_7Zn_4Al_2$	21/13		
	SrTl	2.5			$Li_{10}Pb_3$	22/13		
	AlNd	3.0			$Li_{10}Ag_3$	13/13		
	PdCu	0.5						
	TlSb	4.0						
	TlBi	4.0						

II. A NEW SYSTEM OF METALLIC VALENCES

The Hume-Rothery valences described above have the values zero for manganese, iron, cobalt, and nickel, one for copper, two for zinc, three for gallium, etc. For the metals from copper on these values correspond to the assumption that all electrons outside of a completely filled *3d* sub-shell are valence electrons. A new valence system for the transition metals was proposed in 1938[14] and has been recently applied in the discussion of values of interatomic distances in metals and intermetallic compounds.[15] This system of valences depends primarily on the interpretation of values of the saturation magnetic moment of ferromagnetic metals. It represents an alternative interpretation of these magnetic moment data to that given by Mott and Jones, Slater, and other investigators. The previous interpretation may be illustrated by the consideration of nickel. The saturation magnetic moment of nickel is 0.61 Bohr magnetons per atom. Nickel has atomic number 28, and it might be expected that it would have a completed *3d* sub-shell, with no outer electrons. The value 0.61 magnetons for the magnetic moment is explained by saying that there is a transfer of 0.61 electrons per atom from the *3d* sub-shell to a bonding Brillouin zone, formed by *4s* electrons, which contribute little to the magnetic properties, and that the deficiency of 0.61 electrons in the *3d* sub-shell is responsible for the magnetic properties. (On this basis the Hume-Rothery valence of nickel might well be expected to be 0.6 instead of 0.) The observed saturation magnetic moment of cobalt, 1.71 Bohr magnetons, is similarly accounted for by the assumption that essentially the same number of electrons, 0.71 per atom, are used as binding electrons in a *4s* Brillouin zone, leaving a deficiency of 1.71 in the *3d* sub-shell. The moment observed for iron, however, offers some difficulty, in that its value, 2.22 magnetons, would indicate, on a straightforward extension of the argument, that only 0.22 electrons per atom were involved in the metallic binding. Because the mechanical properties seemed difficultly reconcilable with this assumption, Slater[16] arbitrarily assumed, instead, that the Hund rules are no longer applicable to iron and that the magnetic moment for the partially filled *3d* sub-shell is not to be calculated in the usual way, as the difference between the maximum occupancy of the sub-shell, 10, and the number of electrons present.

The alternative explanation proposed in 1938 for these values is that the 9 orbitals, five *3d*, one *4s*, and three *4p*, per atom are to be hybridized and divided into three classes. The first class of hybrid orbitals is the stable bonding orbitals, the number of which is approximately 5.78 per atom. The second class of orbitals, stable atomic orbitals, presumably *3d* orbitals, is present to the extent of about 2.44 per atom. The third class, 0.78 per atom, consists of unstable orbitals that are not utilized except at and beyond the subgroup IV*b* of the periodic table. With these assumptions the sequence of metals potassium, calcium, scandium, titanium, and vanadium use, respectively, 1, 2, 3, 4, and 5 electrons per atom in forming bonds, their metallic valences being then equal to the maximum normal chemical valences of the elements. If only 5.78 bonding orbitals are available, chromium would be considered to form 5.78 bonds, and to retain 0.22 electrons per atom in the stable atomic orbitals. Manganese and iron would similarly contain 5.78 bonding electrons per atom, with 1.22 and 2.22 unpaired electrons occupying the stable atomic orbitals; this, then, accounts for the observed saturation magnetic moment of 2.22 for iron. A similar explanation applies also to the alloys of iron and chromium and of iron and vanadium, for which experimental values are indicated in Fig. 1.

When the effective atomic number becomes a little greater than the value for iron, however, the stable atomic orbitals are occupied by one electron per orbital, and further electrons can enter this set of orbitals only by becoming paired; accordingly, the magnetic moment begins to fall, as is indicated by the experimental data. The magnetic moment drops to the value 1.7 for cobalt and 0.6 for nickel, and to zero at a point 60 percent of the way between nickel and copper.

The numbers 5.78 and 2.44 were obtained in 1938 by the analysis of these magnetic data. It is seen from Fig. 1 that the experimental points are not precisely represented by straight lines with slope +1 and −1, and that, accordingly, there is some uncertainty in the construction of these lines and, hence, in the number of bonding orbitals and the number of stable atomic orbitals deduced from them. The full lines in Fig. 1 are those selected in 1938. The dashed lines, which

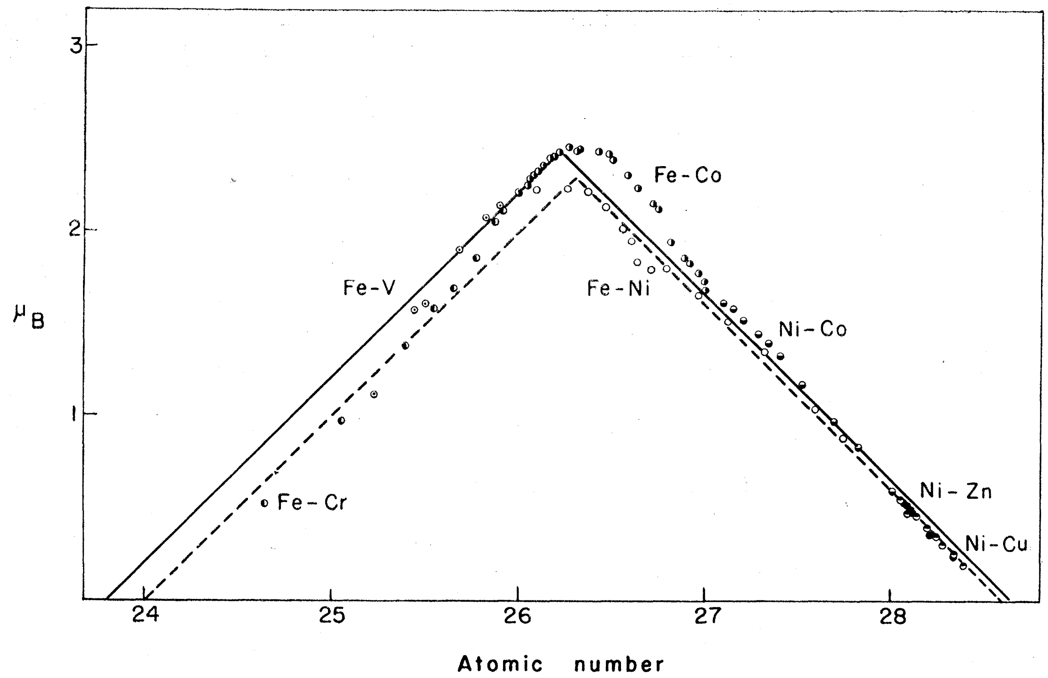

FIG. 1. Experimental values of saturation magnetic moment, in Bohr magnetons per atom, for ferromagnetic metals and alloys, as function of average atomic number.

may be considered to represent the data about as well, correspond to 6 bonding orbitals per atom and 2.30 atomic orbitals per atom. It is not possible to obtain satisfactory agreement with the experimental points by the use only of integral numbers of orbitals per atom.

In the papers referred to above it is pointed out that the mechanical properties of the transition elements and the distances between atoms in metals and intermetallic compounds are well accounted for by these considerations. In the following sections of the present paper a discussion is given of the number of valence electrons by the Brillouin polyhedron method, and it is shown that the calculations for the filled-zone alloys such as the γ-alloys provide further support for the new system of metallic valences.

Let us review the calculation of the number of electrons in successive Brillouin zones. The calculation has as its starting point a distribution of free electrons. In a volume V to which the electrons are restricted the most stable pair of electrons occupies the lowest energy levels, with nearly zero kinetic energy, and correspondingly long wave-lengths. As the number of electrons in the metal increases, continually higher energy levels are occupied until finally there occur electrons with wave-lengths having the value corresponding to a Bragg reflection at 90° incidence from a crystallographic plane with the largest interplanar spacing present in the crystal. The value of the wave-length is found from the Bragg equation $n\lambda = 2d \sin\theta$ to be equal to $2d_{hkl}$, for $n = 1$ and $\sin\theta = 1$.

A very simple calculation can be made of the number of electrons with energy less than this value at which strong perturbation begins. The volume in phase space corresponding to energy values equal to or less than this critical value is $(4/3)\pi p^3_{\max} V$. There is one quantized state per volume h^3 in phase space, and two electrons occupy each quantized level; hence, the number of electrons is $2/h^3 \cdot (4/3)\pi p^3_{\max} V$. This equation can be simplified by replacing $p_{\max}$ by its value as given by the deBroglie expression, $p_{\max} = h/\lambda_{\min}$, which is in the case under consideration equal to $h/2d_{hkl}$. The number of electrons contained within this momentum sphere then becomes $N = \pi V/3d_{hkl}^3$. In a cubic crystal the interplanar spacing d_{hkl} is equal to $a_0/(h^2+k^2+l^2)^{\frac{1}{2}}$. If we

TABLE II. X-ray reflection data for γ-brass (Cu_5Zn_8) and calculated electron densities.

hkl	Σh^2	Square of structure amplitude S^2	Number of electrons per unit cell: Brillouin polyhedron	Valence electrons (H-R)	(P)
110	2	0.1			
200	4	0.0			
211	6	0.1			
220	8	0.0			
310	10	0.1			
222	12	7.2	72		
321	14	1.1			
400	16	0.0			
330	18	78.3	108 } 90	84	—
411	18	31.7	97.2		
420	20	0.5			
332	22	8.4	148		
422	24	5.5	144		
510	26	3.3	(194)		
431	26	0.5			
521	30	0.7			
440	32	2.2	(256)		
433	34	0.5			
530	34	0.8			
600	36	24.0	432 } 255.60	—	250.88
442	36	8.4	291.60		
611	38	3.4	(326)		
532	38	1.5			
620	40	0.1			
541	42	0.1			
622	44	1.3			
631	46	8.0			

introduce this expression and replace V by a_0^3, we find that the number of electrons contained within the momentum sphere per cubic unit cell is

$$N=\frac{\pi}{3}(h^2+k^2+l^2)^{\frac{3}{2}}.$$

The number of electrons in a Brillouin zone is that given by the volume in momentum space represented by a polyhedron with faces corresponding to the crystallographic indices of the perturbing crystallographic plane and circumscribed about the minimum sphere. The volume of the Brillouin polyhedron is accordingly somewhat larger than that of the minimum sphere; it can be determined by geometrical calculation.

III. THE GAMMA-ALLOYS

The structure of γ-brass was determined by Bradley and Thewlis.[5] This structure may be derived from a unit consisting of 27 body-centered cubes, containing altogether 54 atoms, by removing two of the atoms, at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ of the large cube, and slightly rearranging the remaining 52 atoms. Since this structure is essentially a superstructure of $A2$ (in the nomenclature of the Strukturbericht) it would be expected that only a few of the crystallographic planes would reflect strongly. This expectation is borne out by observation, as can be seen from Table II, where the intensities of reflection for crystallographic planes out to $\Sigma h^2=h^2+k^2+l^2=46$ are given. (These values are calculated for γ-brass, Cu_5Zn_8, from the structure reported by Bradley and Thewlis; the calculated values of the stronger reflections are in excellent agreement with the observed values.)

The first set of strong reflections occurs at $\Sigma h^2=18$. As was stated above, Jones found the Brillouin polyhedron defined by the corresponding forms {330} and {411} to have the volume $45/a_0^3$, giving an electron density of 90 electrons per unit cell. The next set of strong reflections occurs at $\Sigma h^2=36$. We have found it possible to construct a Brillouin polyhedron defined by the corresponding forms {600} and {442}. This polyhedron, shown in Fig. 2, has a volume of $(9^3/5-18)/a_0^3=127.800/a_0^3$, enclosed by its 30 faces, leading to an electron density of 255.600 electrons per unit cell. The new metallic valences 5.44 for copper and 4.44 for zinc lead to 250.88 electrons per unit cell (containing 4 molecules of Cu_5Zn_8), in very close agreement with the value calculated for the second Brillouin polyhedron. The fill of the Brillouin polyhedron is $250.88/255.6=98.5$ percent, and accordingly this calculation gives considerably better explanation of the filled-zone properties of the alloys than the Jones treatment, where a fill of only $84/90=93.5$ percent was obtained.

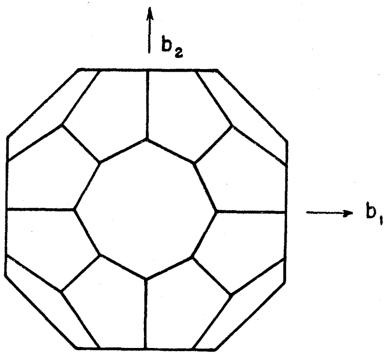

FIG. 2. The Brillouin polyhedron for forms {442} and {600}, an important one for γ-brass and other γ-alloys.

TABLE III. X-ray reflection data for β-manganese structure (Ag_3Al) and calculated electron densities.

			Number of electrons per unit cell			
					Valence electrons	
hkl	Σh^2	Calculated intensity	Brillouin polyhedron		(H-R)	(P)
221	9	86	32.4		30	—
310	10	48				
311	11	26				
222	12	0.8				
320	13	0.7				
321	14	7				
400	16	0.02				
322	17	0.02				
410	17	0.7				
330	18	0.01				
411	18	2.1	97.21	96.13	—	96.60
420	20	4	111.11			
421	21	0.3				
332	22	1.3				
422	24	1.6				
430	25	2.3				
431	26	20				
510	26	4				
333	27	0.05				
511	27	4				

Inasmuch as the inscribed sphere corresponds to only 226 electrons per unit cube, it seems likely that the density of energy levels in momentum space has become small at 250.88, possibly small enough to provide a satisfactory explanation of the filled-zone properties. However, there exists the possibility that the Brillouin polyhedron is in fact completely filled by valence electrons. If there are 255.6 valence electrons per 52 atoms at the composition Cu_5Zn_8, and if the valence of copper is one greater than the valence of zinc, then it is possible to determine values of the metallic valences of these elements from the assumption that the Brillouin polyhedron is filled. These values are found to be 5.53 for copper and 4.53 for zinc. The accuracy of the determination of the metallic valences from magnetic properties is not great enough to exclude these values; in fact, the valence for copper calculated by the assumption that the full line in Fig. 1 is to be accepted is 5.44 and that calculated from the assumption that the dashed line is to be accepted is 5.60, so that the value 5.53 given by the Brillouin-polyhedron calculation for γ-brass lies within these limits. It may accordingly be said that the Brillouin-polyhedron calculation for γ-brass provides substantiation of the new set of metallic valences.

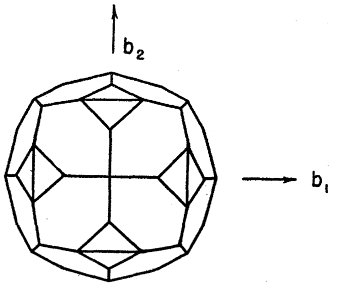

FIG. 3. The Brillouin polyhedron {411} {420}, for β-manganese, Ag_3Al, and $CoZn_3$.

It may be noted that the Brillouin polyhedron used in this calculation corresponds to the only strongly reflecting planes in the entire range $26 \leqslant \Sigma h^2 \leqslant 46$. Thus the Brillouin polyhedron is, in effect, isolated from interference by any neighboring crystallographic planes.

It is interesting to note that the same electron number, 250.88 electrons per unit cell, is found not only for the compounds similar in composition to Cu_5Zn_8 (Cu_5Cd_8, Ag_5Zn_8, Ag_5Cd_8, Au_5Zn_8, Au_5Cd_8, Au_5Hg_8) but also for other γ alloys involving the metals of the *B* subgroups of the periodic table, such as Cu_9Ga_4, Cu_9In_4, $Cu_{31}Sn_8$, and $Ag_{31}Sn_8$. In fact, it can be easily shown that the constancy of the electron-atom ratio for all of these compounds, with the compositions as given here, holds for any set of valences in which the successive elements in the periodic table differ in valence by either +1 or −1. The Hume-Rothery valences correspond to an increment in valence of +1 with increase in atomic number and the new valences to an increment of −1.

The γ-phase is homogeneous in the copper-zinc system over the range of compositions of 60 to 69 atomic percent of zinc. These limits correspond to 251.68 and 247.00 electrons per unit cell, respectively. It was found by Lane[17] that at room temperature the diamagnetic susceptibility of γ-brass is approximately a linear function of the zinc content over the range 60 to 67 weight percent (59–65 atomic percent) increasing from 0.25×10^{-6} to 0.80×10^{-6} in this interval. He also found that the magnetic susceptibility of alloys with about 60 atomic percent zinc, corresponding closely to the composition Cu_5Zn_8, changes very little with temperature from 0 to 400°C, whereas that of the samples containing larger amounts of zinc decreases rapidly with increasing temperature, the values for all alloys being 0.3×10^{-6} at approximately 800°C. It seems likely that the alloys with a filled Brillouin zone behave normally with respect to their diamagnetic properties, whereas abnormally large diamagnetism results from a small defect in the zone.

In the copper-tin system the γ-phase is homogeneous between 20.8 and 22.3 atomic percent tin. This corresponds to a change from 250.43 to 248.09 electrons per unit cell, using the valences 5.44 and 2.44 for copper and tin, respectively. If we adopt the slightly higher values 5.53 and 2.53 suggested by the values required for a completed polyhedron in γ-brass, we obtain 254.81 and 252.77, corresponding to 99.85 and 98.9 percent filling of the polyhedron.

Whereas the compounds such as Cu_9Ga_4 with gallium and its congeners give similar agreement with the Brillouin-polyhedron calculations, the corresponding compounds Cu_9Al_4 and Ag_9Al_4, which have the same numbers of electrons according to the Hume-Rothery treatment, lead to only 243.84 electrons per unit cell with the new valences. The compounds M_5Zn_{21}, M_5Cd_{21}, and M_5Hg_{21}, with M = Fe, Co, Ni, Rh, Pd, or Pt, similarly show with the new valences the low value 244.28 electrons per unit cell. It seems probable that in these compounds, involving a metal of the transition group and a metal of the ascending branch of the transition group, in which the metallic valence can be increased by the removal of an electron, the phenomenon of electron transfer occurs, some electrons being removed from the zinc atoms and assigned to the iron atoms (in Fe_5Zn_{21}). The valence of the iron atom is not changed by its negative charge, whereas that of the zinc atom is increased by the removal of electrons, and accordingly added stability of the compounds can be achieved in this way. To produce a filled zone about $\frac{1}{4}$ electron must be removed from each zinc atom in Fe_5Zn_{21} and 1 electron added to each iron atom. A similar transfer of electrons from copper to aluminum produces a filled Brillouin zone for the compound Cu_9Al_4.

IV. THE BETA-MANGANESE STRUCTURE

The β-modification of metallic manganese, stable at higher temperatures, has a rather complex cubic structure[18] containing 20 atoms in the unit cube. Westgren and Bradley[19] found that the compound Ag_3Al has an x-ray diffraction pattern substantially identical with that of β-manganese. They discussed the possibility that the 20 atomic positions per unit cube in the

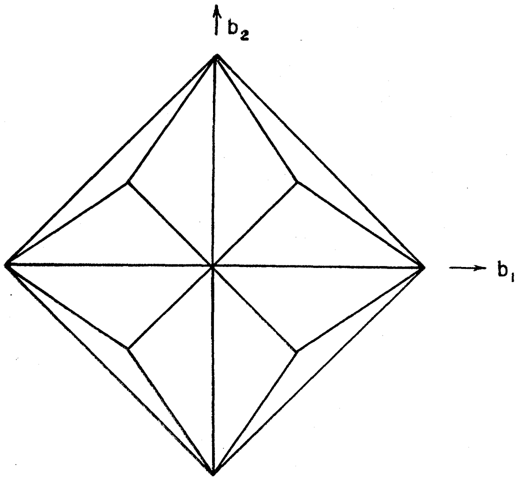

FIG. 4. The Brillouin polyhedron {442}, for α-manganese.

TABLE IV. X-ray reflection data for α-manganese and calculated electron densities.

			Number of electrons per unit cell	
hkl	Σh^2	S^2	Brillouin polyhedron	Valence electrons (P)
110	2	0		
200	4	0		
211	6	0		
220	8	2		
310	10	0		
222	12	5		
321	14	2		
400	16	54		
330	18	217	108 } 90	
411	18	242	97.2	
420	20	0		
332	22	125	148 } 134	140 (Mg_3Al_2)
422	24	52	144	
431	26	31		
510	26	13	194	
521	30	5		
440	32	3		
433	34	6		
530	34	3		
442	36	17	291.60	293.76
600	36	1		
532	38	9		
611	38	6		
620	40	4		
541	42	2		
622	44	35		
631	46	5		
444	48	275		

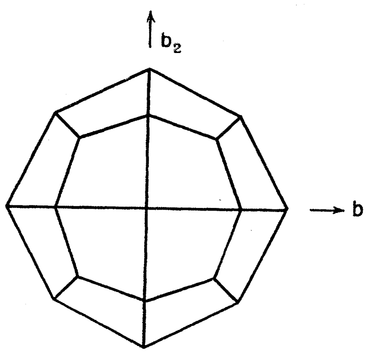

Fig. 5. The Brillouin polyhedron {422}, for $Mg_{17}Al_{12}$.

β-manganese structure are occupied by silver and aluminum atoms distributed essentially at random. This statistical distribution was verified by the x-ray data for Ag_3Al by Fagerberg and Westgren[20] and was also extended to Au_3Al and Cu_5Si by them. The data of these investigators for Ag_3Al are reproduced in Table III. It is seen that the first strong x-ray reflections are those from the forms {221} and {310}, which were used by Mott and Jones to set up a Brillouin polyhedron containing, as was mentioned above, 32.4 electrons per unit cell, in fair correspondence with the 30 electrons required by the Hume-Rothery ratio 3/2.

The new values of the metallic valences lead to 96.60 electrons per cell for Ag_3Al and Au_3Al. In the region $16 \leqslant \Sigma h^2 \leqslant 24$ there are only two strongly reflecting forms, {441} and {420}. These give separate Brillouin polyhedra containing 97.21 and 110.0 electrons, respectively; they combine to give a truncated polyhedron, shown in Fig. 3, which contains 96.13 electrons per unit cell. This value is in good agreement with the value 96.60 calculated from the metallic valences. It might be mentioned, however, that a somewhat larger value might be expected from the metallic valences, since presumably the conditions are satisfactory for the phenomenon of electron transfer to occur.

The compound Cu_5Si, which with the older valences has the same calculated electron number as Ag_3Al, leads with the new system to a different electron density, 104 electrons per unit cell.

It was reported by Fagerberg and Westgren[20] that the compound $CoZn_3$ also crystallizes with the β-manganese structure. The electron number calculated from the valences 5.78 for cobalt and 4.44 for zinc is 95.50 electrons per unit cell, which is only 0.7 percent less than required to fill the Brillouin polyhedron.

A notable shortcoming in the earlier system was the failure to provide a consistent treatment for β-manganese itself, because of the arbitrary assignment of zero valence to manganese and the other transition elements. In the new system of metallic valences the transition metals in general have the valence 5.78, but a detailed examination of the interatomic distances[15] led to the conclusion that two essentially different kinds of manganese atoms are present in β-manganese, 8 atoms in the unit cube with valence 5.78 (or 6) and 12 with valence 4, leading to 94.24 (or 96) electrons per unit cell. We accordingly conclude that the stabilization of the β-manganese structure for β-manganese itself as well as for the compounds Ag_3Al and Au_3Al results in part from the filling of the Brillouin polyhedron.

V. THE ALPHA-MANGANESE STRUCTURE

α-Manganese, like β-manganese, has physical properties of brittleness and low electrical conductivity that indicate a filled-zone structure. It could not be treated under the old system of valences, because of the zero valence assigned to the element. The structure of α-manganese is very complicated, the unit cell containing 58 atoms arranged compactly together.[21]

The x-ray data for α-manganese as reported by Preston are given in Table IV. It is seen that there is a pair of strong reflections with $\Sigma h^2 = 18$, leading to a Brillouin polyhedron containing 90 electrons per unit cube. Another pair of strong reflections occurs with $\Sigma h^2 = 22$ and 24, which together produce a truncated polyhedron containing 134 electrons. Then there occurs the reflection {442}, which leads to 291.60 electrons per unit cell (see Fig. 4). It may be noted that this polyhedron is related to that discussed above for the γ-alloys; with α-manganese, however, the {600} reflection has very small intensity, and accordingly is not considered to truncate the {442} polyhedron.

It was pointed out by Bradley and by Hume-Rothery[22] that the nature of the α-manganese structure suggests that there are manganese atoms present of two different sizes, and a study of interatomic distances[15] led to the conclusion that of the 58 atoms in the unit cell 24 have the normal valence 5.78 (or 6) and 34 a lower valence of about 4 or 4.5. The actual values indicated for the different kinds of manganese of lower valence are 2 MnI, 3.52; 8 MnII, 4.70; 24 MnIII, 4.60. The electron number calculated with valences 5.78 and 4 is 274.72, whereas that calculated for the valences 5.78, 3.52, 4.70, and 4.60, suggested by the interatomic distances, is 293.76. It is seen that, to within the uncertainty of the valence values, the electron number is such as to correspond to the filling of the Brillouin polyhedron {442}.

Only one intermetallic compound has so far been reported to have the α-manganese structure. This is the compound with approximate formula Mg_3Al_2, found by Laves, Löhberg, and Rahlphs[23] to have a structure with 58 atoms in the unit cell. These investigators suggested that the formula is $Mg_{17}Al_{12}$, the larger magnesium atoms then being analogous to the large low-valent manganese atoms in α-manganese, and the smaller aluminum atoms analogous to the smaller high-valent manganese atoms in this structure. The electron number for $Mg_{17}Al_{12}$ is 140 electrons per unit cell. This does not correspond very closely to the content of the Brillouin polyhedron, which is 134 for the {332} polyhedron truncated by {422} (Fig. 5). These polyhedra independently contain 148 and 144 electrons per unit cell, respectively.

VI. THE BETA ALLOYS

The β-alloys are different in nature from the γ-alloys and the α-manganese and β-manganese structures discussed above, in that they are not complex structures, but are simple, being based upon the body-centered arrangement. β-Brass, for example, has either a disordered structure, above 480°K, the copper and zinc atoms in essentially equal number being distributed largely at random over the points of a body-centered cubic lattice, or an ordered structure, below 300°K, with copper and zinc at the positions 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, respectively, of the cubic unit. Moreover, the physical properties of β-brass are not those that indicate a filled zone structure.

It seems likely that the assumption of the β-brass structure is determined mainly by factors other than the ratio of valence electrons to atoms. Nevertheless, it is a fact that the ratio of valence electrons to atoms calculated with the Hume-Rothery valence is 3/2 for more than one-half of the intermetallic compounds reported to have this structure, and it seems likely that stabilization is due in part to this ratio.

For CuZn the number of valence electrons in the unit cube is 3, in case that the older valences of 1 and 2 are accepted for copper and zinc, respectively, and 9.88 with the newer valences 5.44 and 4.44. The Brillouin polyhedra for the body-centered cubic arrangement contain 4, 8, 12, $\cdots$ electrons per unit cell, whereas those for the $B2$ structure, corresponding to an ordered arrangement of atoms at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, contain 2, 4, 6, 8, 10, 12, $\cdots$ electrons per unit cell. In either case the Hume-Rothery number of valence electrons, 3, does not correspond to a Brillouin zone. On the other hand, an ordered arrangement of atoms with different scattering powers for electrons in the positions 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ would cause a perturbation of energy levels such as to tend to stabilize a structure with 10 valence electrons per unit cell. In case that the scattering powers for electrons of the two atoms were not very greatly different, the resultant perturbation would not be great enough to separate the Brillouin zone from the succeeding zone, and the alloy would retain metallic properties; the perturbation would, however, have the effect of depressing the energy levels occupied by the 10 electrons per unit cell, and would accordingly tend to stabilize the ordered structure for the alloy.

It has been found by x-ray investigation that many of the β-alloys have an ordered structure sufficiently pronounced to produce x-ray reflections involving the difference in scattering powers of the atoms at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. For these alloys the stabilization of ten electrons per unit cell would be expected, as discussed above. When the alloy changes from an ordered to a disordered phase on increase in temperature, there might still remain sufficient short-range order to produce this stabilization to some extent, even though not enough to give rise to x-ray reflections, the atoms having much smaller scattering powers for x-rays than for the slow electrons in the lattice. Similarly, stabilization of the alloy

CuZn would be expected, because the scattering powers of the two atoms for slow electrons in the lattice are probably considerably different, even though the scattering powers for fast electrons and for x-rays are very nearly the same.

VII. THE SIGNIFICANCE OF THE BRILLOUIN-POLYHEDRON CALCULATIONS

It is seen from the above considerations that there is what seems to be significant agreement between the electron numbers filling important Brillouin polyhedra and the number of valence electrons provided by the new system of metallic valences for the γ-alloys, β-manganese and alloys of similar structure, and α-manganese. There is also agreement, somewhat more approximate, between the electron numbers given by other Brillouin polyhedra and those provided by the older valence system. The agreement in each case can hardly be accidental, since the Brillouin polyhedra correspond to the planes giving the strongest x-ray reflections. It seems likely that both series of electron numbers are significant, but an understanding of their significance may not be obtained until a more penetrating theory of the structure of metals and alloys has been developed.

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