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Do metallic quasicrystals and associated Frank and Kasper phases follow the Hume Rothery rules?

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(14. XII. 1987)

In honor of Martin Peter's 60th birthday.

Abstract. The electronic structure of metallic quasicrystals and associated Frank and Kasper phases is discussed and the energetics of such phases are compared to those of simpler alloy phases. Standard elementary models derived from the Hume Rothery rules are used for some elementary remarks.

Introduction

The metallic quasicrystalline phases [1] and associated long period Frank and Kasper phases [2] obviously arise from a frustration effect, or a compromise, between opposite factors. The short range close packing of atoms favors tetrahedral bonding which however cannot cover without distortions a large volume in space, or *a fortiori* build a periodical crystal.

A detailed discussion of the stability of such phases thus requires a delicate study of the interatomic interactions involved. This might possibly be done, case by case, using the standard (local density) computer methods [3], at least for Frank and Kasper phases with not too large periods. This is not the point of view taken here. Inspired by the empirical observations by Hume Rothery [4], approximate models have been developed for the study of various kinds of metallic alloys and compounds. We just want to discuss here what such models can tell us about the more complex phases involved here and about their stability. We shall keep to fairly general remarks, leaving out most of the possible applications to specific cases.

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As first pointed out by Hume Rothery,

1. Metallic alloys, either in solid solutions or in compounds form, mix fairly freely elements with comparable electronegativities and 'suitable' relative sizes: comparable sizes for substitutional alloys, small sizes for interstitial solute elements, specific size ratios for Laves phases [5] . . .
2. Alloys of this kind tend to form specific phases for definite average valence electrons per atom ratio.
3. *f*-electrons of rare earth elements do not count in this ratio. When appearing as minority solute components, transitional elements seem to act as having zero or even negative valences, i.e., the *d* shells do not take part in the count and seem even to absorb valence electrons of the matrix.

This leads us to discuss three cases in turn which correspond to classical families of metallic alloys and compounds.

- *nearly free valence electrons*, involving normal metals at the beginning of the *sp* or *sd* series and also most rare earth metals. Here, the valence electrons are but weakly scattered by the atoms [6].
- *narrow bands*, involving the *d* bands of transitional metals [7] or the *6d–5f* bands of heavy metals [8]. Here, the corresponding electrons can be treated approximately in the limit of linear combination of atomic orbitals.
- mixtures of these two families which involve *resonant (p, d or f) states*. The simplest and best known case is that of virtual bound *d* levels of transitional solute elements in normal metals [9]. But other examples are resonant *p* states of normal solute elements in transitional matrices [10] or resonant *f* states of some rare earth [11] or of heavy metals dissolved in an *spd* matrix [13].

What we have to say on these various cases is nothing especially new. It fits with the general characteristics of the three families and mainly shows that the detailed analysis of these structures do not necessarily involve the same sort of interatomic forces. Indeed the mere possibility of using additive interatomic forces is in question in most cases.

This paper concentrates on the Hume Rothery rules concerning the average electron per atom ratio. It will therefore assume that the cases considered follow the Hume Rothery rules concerning size and electronegativity.

A. Nearly free electrons in normal and rare earth alloys and compounds

In this family, the average number of valence electrons per atom ratio seems to dominate the so-called Hume Rothery–Jones phases, when size and electronegativity factors are favorable. It has indeed been argued repeatedly that quasicrystals and Frank and Kasper phases of this family followed the Hume Rothery–Jones rule [13, 14].

According to Jones [15], a special stability of the alloy occurs when the Fermi

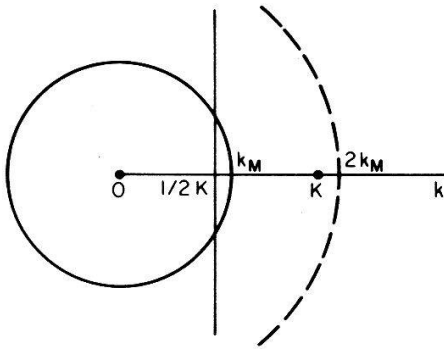


Figure 1
Condition for a Hume Rothery–Jones phase.

sphere containing the valence electrons just touches strong Brilluoin zone boundaries, with large gaps $|V_k|$ (Fig. 1). We first recall Blandin's treatment of the crystal case [16], before discussing its extension to solid solutions and quasicrystals.

B. Blandin's approach for metals and stoichiometric compounds

Blandin's treatment of this problem is historically the first correct one, and also is very transparent in the relation between the pictures in real and reciprocal spaces, in the approximations made, in the exact consequences for stability [17–19].

The treatment starts with the *kinematic* approximation, where one assumes that every electron wave in the alloy can be analyzed as one plane wave $|\mathbf{k}\rangle$ plus small contributions from other plane waves:

$$|\psi_{\mathbf{k}}\rangle \propto |\mathbf{k}\rangle + \sum_{\mathbf{K}} a_{\mathbf{k}}^{\mathbf{K}} |\mathbf{k} + \mathbf{K}\rangle. \quad (1)$$

The classical (iron degenerate) perturbation theory gives

$$a_{\mathbf{k}}^{\mathbf{K}} \propto \langle \mathbf{k} + \mathbf{K} | \sum_i V_i | \mathbf{k} \rangle = \sum_i V_{i\mathbf{K}} e^{i\mathbf{K}\mathbf{R}_i} \quad (2)$$

where the atomic potentials V_i , at sites \mathbf{R}_i , have Fourier components $V_{i\mathbf{K}}$.

Within the *same* approximation, one can develop the total electronic energy of the alloy in successive powers of V_i . The first term which depends on the relative positions of the atoms is a second order term ΔE , which will obviously be the sum of pair interactions, where the two scattering atoms i, j can be thought as two impurities in an otherwise free electron gas. A well-known result of electrostatics (of Appendix A) gives [20, 21]

$$\Delta E = \frac{1}{2} \sum_{i>j} V_i \rho_j^0 \quad (3)$$

where ρ_j^0 is the charge density of the inner ion j , while V_i is the total potential of atom i , including the screening by the valence electrons. Introducing the dielectric constant ϵ_K of the free electrons gas, which depends on the wave vector

K of the perturbation, this can be written

$$\Delta E = \frac{1}{2} \sum_{\mathbf{K}} \frac{K^2}{4\pi\epsilon_K} \sum_{i>j} V_{ik}^0 V_{jk}^0 e^{i\mathbf{K}\mathbf{R}_{ij}}, \quad (4)$$

where V_{iK}^0 is the Fourier transform of the potential of the inner ion i .

In crystals, one can split the summation over atomic sites into a summation over lattice periods n and a summation over the atomic sites i of a unit cell with

$$\sum_{\mathbf{R}_n} e^{i\mathbf{K}\mathbf{R}_n} = N\delta(\mathbf{K} - \mathbf{K}_{RR}). \quad (5)$$

ΔE reduces to

$$\Delta E = N \sum_{\mathbf{K}_{RR}} F_{\mathbf{K}_{RR}} \quad (6)$$

where

$$F_{\mathbf{K}} = \frac{K^2}{8\pi\epsilon_K} \sum'_{i>j} V_{iK}^0 V_{iK}^0 e^{i\mathbf{K}\mathbf{R}_{ij}}. \quad (7)$$

$F_{\mathbf{K}}$ is a form factor for the atomic composition of one crystal cell, and \mathbf{K}_{RR} are the periods of the reciprocal lattice.

With the definition of V_i^0 , the factor $\sum'_{i>j} V_{iK}^0 V_{iK}^0 e^{i\mathbf{K}\mathbf{R}_{ij}}$ is a smoothly varying function of \mathbf{K} , while ϵ_K possesses a well-known logarithmic anomaly at $K = 2k_M$ (Fig. 2). Thus each period \mathbf{K}_{RR} in reciprocal space contributes to the energy a term $\Delta E_{\mathbf{K}}$ which has also a logarithmic anomaly at $K = 2k_M$ (Fig. 3).

If the Fermi level falls in the vicinity of the Brillouin zone limit corresponding to period \mathbf{K}_{RR} , the valence electron gas thus exerts inner pressure to bring the Fermi sphere just beyond the condition $2k_M = K_{RR}$. This pressure induces it to cut slightly the corresponding Brillouin zone boundary (Fig. 1).

In fact, in a more complete discussion of the phase diagram, one must plot the energy ΔE as a function of the composition or, here, of $2k_M$, and compare the variations of $\Delta E(2k_M)$ for different possible phases. Figure 4 shows that a given phase (here β) can appear or not, depending on small variations of the relative positions of these curves for the various phases α, β, γ possible. If such a

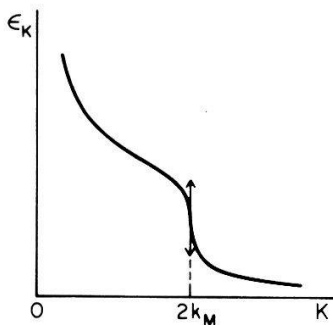


Figure 2
Variation of ϵ_K with K .

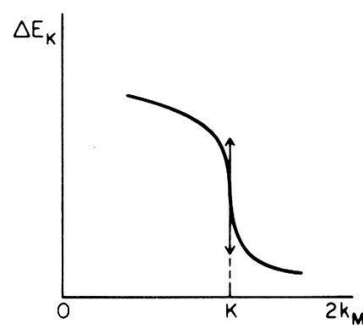


Figure 3
Variation of ΔE_K with K .

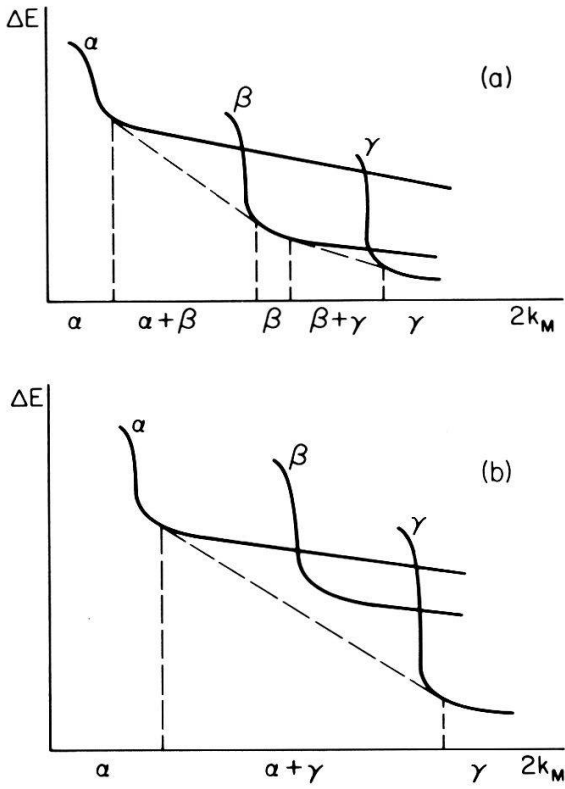


Figure 4
Relative positions of $\Delta E(2k_M)$ for three possible phases α, β, γ inducing two different phase diagrams: (a) α, β, γ ; (b) α, γ (no β phase).

phase appears, the Kohn anomaly [22] in $\Delta E(2k_M)$ makes it indeed appear for the condition $K \geq 2k_M$ pictured Fig. 1.

Now of course a proper treatment of electronic waves near Brillouin zone boundaries should start from a more correct *dynamical* approximation, where at least two plane waves are assumed to have large amplitudes:

$$|\psi_{\mathbf{k}}\rangle \approx A |\mathbf{k}\rangle + B |\mathbf{k} + \mathbf{K}\rangle + \sum_{\mathbf{K}' \neq \mathbf{K}} a_{\mathbf{k}}^{\mathbf{K}'} |\mathbf{k} + \mathbf{K}'\rangle. \tag{8}$$

Indeed only this approach gives the correct behavior of $\mathbf{E}(\mathbf{k})$ of $|\psi_{\mathbf{k}}\rangle$ near a Brillouin zone boundary, while the kinematic approximation (1) gives divergences of $E(\mathbf{k})$ (Fig. 5). However, as was stressed by Pick and Blandin [23], we are only interested here in an *integral* property of the $E(\mathbf{k})$, where one sums contributions up to a Fermi level which, in 3-dimensions, only falls in the gap over a very limited area of the Fermi sphere. In most directions, it is below or above the gap, in a position such that the divergencies do not appear or cancel out. If then one

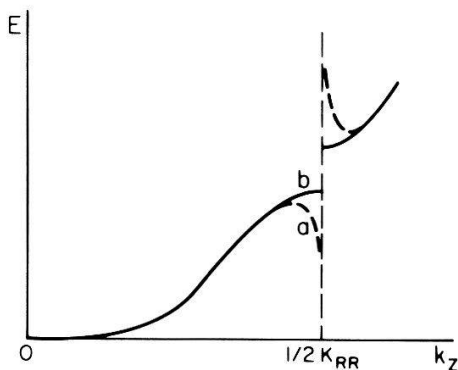


Figure 5
Variation of $E(\mathbf{k})$ near a Brillouin zone boundary: (a) kinematic; (b) dynamical approximation.

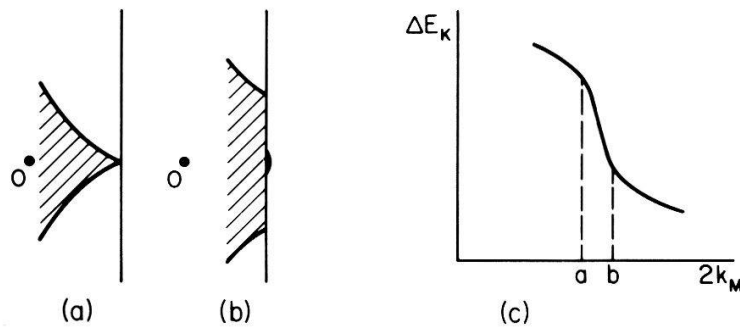


Figure 6 Two values of E_M for which one expects an anomaly in ΔE_K in the dynamical approximation (a, b) and the corresponding changes of slope of $\Delta E_K(2k_M)$ (c).

computes correctly such an integral property in the dynamical approximations and then develops the result to second order in the V_{iK} , one finds the same result as in the kinematic approximation, which is therefore valid as a *perturbation development*.

It is worth pointing out at this stage that in this approximation ΔE_K has a logarithmic anomaly. For *finite* values of V_K , thus of the gap (Fig. 5), one expects on the other hand ΔE_K to have two successive ruptures of slope [15]: one when the Fermi surface begins to touch the Brillouin zone boundary; one when it begins to flow over the boundary over the next Brillouin zone (Fig. 6). In the same way, the density of states $n(E)$ has two ruptures of the slope in the dynamical approximation, while it has a double infinity in the kinematic approximation used here (Fig. 7).

However the differences are slight in the region $K \lesssim 2k_M$ of interest. The kinematic approximation is also the only one where a simple treatment of self-consistency can be made, using formula (3). Finally, it has the advantage of analysing the stability in terms of *additive pair interactions* deriving from *central forces* and which can be summed up in direct space. This is especially useful in case of complex or imperfect structures.

A classical study of the pair interaction $V_i\rho_j^0$ shows that it decreases as an

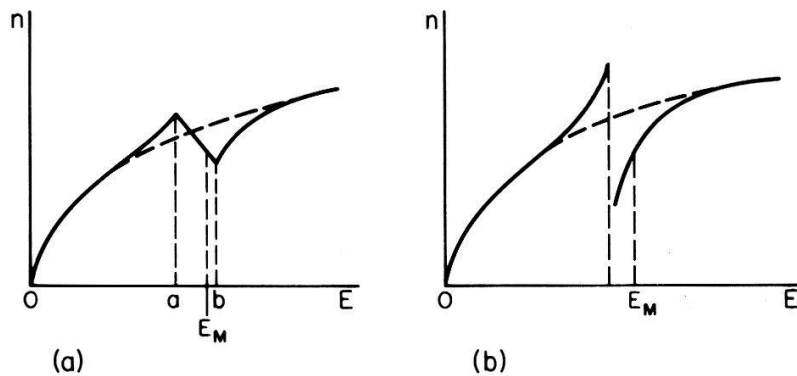


Figure 7 Density of states: 1. dynamical and 2. kinematic approximations.

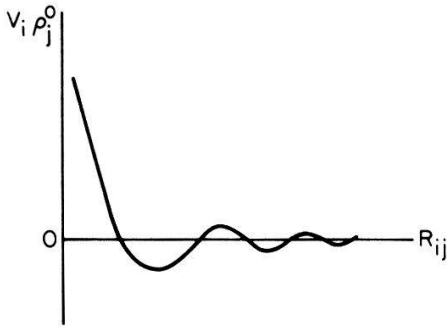


Figure 8
Variation with distance R_{ij} of the pair interaction $V_i \rho_j^0$.

oscillating function of distance R_{ij} [24] (Fig. 8).

$$V_i \rho_j^0 \propto \frac{\cos(2k_M R_{ij})}{R_{ij}^3}. \quad (9)$$

The condition expressed by Fig. 1 is strictly equivalent to stating that these additive pair interactions optimize their (negative) oscillations.

C. Extension to solid solutions, to non-stoichiometric compounds and to quasicrystals

In many instances, the crystal structures considered are not perfect, because two or more chemical elements can occupy, more or less at random, a given site in the lattice cell.

If the scattering potentials of these elements are not too different, one can introduce a virtual perfect crystal where the site considered is occupied by an average potential \bar{V}_i . The local deviation $\delta V_i = V_i - \bar{V}_i$ from this average scatter the electrons incoherently. This reduces their mean free path l ; it produces a continuous scattering background at the expense of a reduction of the coherent scattering intensities, together with a cut off factor $\exp(-R_{ij}/l)$ to the pair interactions (9). However, the corresponding relaxation rate

$$h\nu \simeq \frac{h v_M}{l} \simeq \frac{(\delta V)^2}{E_M} \quad (10)$$

($E_M = \frac{1}{2} m v_M^2$ Fermi energy) produces an energy broadening which does not suppress the gap as long as

$$|\delta V|^2 < |\bar{V}_K E_M| \quad (11)$$

This condition is necessarily fulfilled for the Fermi electrons in the weak scattering limit, where all $|V_K|$'s are small compared with E_M . One can therefore extend the preceding treatment directly to *crystalline solid solutions* and to non-stoichiometric crystal compounds just as for X-rays or fast electrons.

Quasicrystals present a further complication in that one cannot properly describe their structures in terms of a lattice of equivalent cells decorated with atoms. It is however usually believed [25] that, to a good approximation, one can

define a quasilattice comprising two types of cells, and that these cells can be decorated with atoms in a way which is the same for at least most cells. The quasilattice has well defined Fourier transforms, so that equation (5) applies, although the delta functions are now distributed over the whole reciprocal space. The same analysis therefore applies, with again a small continuous scattering background coming now not only from possibilities of atomic solid solutions or non-stoichiometries, but also from small variations of atomic composition or positions from cell to cell.

D. Quantitative applications

This approach shows that if the Fermi sphere just touches a family of Brillouin zone boundaries corresponding to well defined diffractions spots, there will be a *possibility* of observing a corresponding Hume Rothery–Jones compound.

It is tempting to try and relate the relative strengths of the $|V_{\mathbf{k}}|$ to corresponding intensities of diffraction spots observed by X-rays or by fast electron scattering.

This is usually possible only in a qualitative way [14]. The reason is that the V_i 's which scatter weakly the Fermi electrons are *pseudopotentials*, which are different and usually much weaker than the Coulomb potentials involved in fast electron scattering or the corresponding electron densities which scatter X-rays [6, 19]. These pseudopotentials correct for the fact that, but for H and He, the valence electrons are not the states of lowest energy; there is a large kinetic energy correction which compensates most of the short range Coulomb attraction, in a way which varies from element to element.

In general, one can argue that the scattering intensities result from the product of a structure factor of the lattice (or of the pseudolattice) times a form factor of the cell (or of the cells). When one observes only a few families of diffraction spots of large intensities, and if the position of these spots do not vary much with exact composition, one can argue that they are due to a large structure factor of the lattice (or of the pseudolattice), irrespective of the details in the form factors. It is the same structure factor which appears in the diffraction of valence electrons as well as in both X-rays and fast electron diffractions. One can then reasonably argue that the corresponding compounds are Hume Rothery–Jones alloys if the Fermi sphere just touches some of the corresponding Brillouin zone boundaries. In this sense, a number of quasicrystals and Frank and Kasper phases have been said to be Hume Rothery–Jones compounds.

There are however two specific cases where a more quantitative analysis can in principle be made at present.

1. In Frank and Kasper crystal phases of not too large unit cells, where one knows the atomic structure in detail, one could compute directly the different $V_{\mathbf{k}}$ corresponding to the known atomic pseudopotentials. As far as I know, no such computation has been made yet.

2. In compounds where one type of atoms scatters predominantly both the valence electrons and fast electrons (or X-rays), one can compare directly the relative intensities of the potential and pseudopotential values of $V_{\mathbf{k}}$: they are proportional to each other if one neglects the scattering by other atoms.

A case of this kind is the AlLiCu (or AlLiCuMg) alloys [14]. It is obvious that the real Coulomb potential of heavy Cu is much larger than those of light Al, Li or Mg. But it is interesting to notice that the pseudopotential of Cu is also large compared with those of Al, Li, Mg. This is due to the proximity of the Fermi level to the 3*d* shells of Cu, which induces a resonance scattering of Fermi electrons. Indeed the pseudopotentials at Fermi level are roughly in the ratios 6:2:1 for copper, lithium, aluminum, respectively [26].

Table I gives the values of the *K* vectors for the main X-rays diffracting Laue spots of a single quasicrystal of Al₆Li₃Cu, together with the intensity factors $|F_x|^2$ and multiplicities μ , according to recent measurements by Janot [27] which complete earlier ones by Dénoyer [14]. It is seen that $2k_M$ which, for the composition of the alloy studied is equal to $3.12 \pm 0.02 \text{ \AA}$, fulfills the Hume Rothery–Jones condition for the Laue spots which come second in the order of magnitude of $\mu |F_x|^2$.

Two points need to be stressed here.

1. What matters is $\mu |F_x|^2$. A characteristic property of quasicrystals and associated Frank and Kasper phases is that μ is especially large compared with those active in simpler crystal structures [13, 14]. This is related to both the 5-fold symmetry and to the fact that the unit cell is very large (or infinite), so that the active Laue spots are far from being the ones of minimum *K*; they can then have large degeneracies.
2. It is not clear at present whether the samples reported in Table I are quasicrystals or related twinned Frank and Kasper phases [27]. The fact that the Laue spots have a granular structure rather suggests the second case. However the corresponding quasicrystals have Bragg reflections at

Table I
Intensities of Laue spots for Al₆Li₃Cu

$K(\text{\AA}^{-1})$	μ	$ F_x ^2$	$\mu F_x ^2$	n^0
1.480	20	26	520	
2.631	12	40	480	
2.766	30	96	2880	3
3.138	60	61	3660	2
3.252	60	25	1500	
4.476	30	79	2370	4
4.791	60	14	840	
5.262	60	100	6000	1
5.532	120	18	2160	5
5.882	60	27	1620	6

practically the same average values of K , and with a similar pattern of intensities.

It is then clear that the same Brillouin zone boundaries effect stabilizes the two kinds of phases. This seems to be very often the case.

The special stability of these phases can then be viewed as an energetic resonance due to the coherent (weak) scattering of the Fermi electrons by the atoms. They can also be understood as structures where the pair interactions (9) optimize their effects, by a close packing of atoms at distances where a minimum of these interactions arises (Fig. 8).

If this interpretation is correct, the Fermi level should fall in a region where the density of states has values smaller than what is expected for a free electron gas (Fig. 7); this reduction should be of similar amplitude for quasicrystals and associated Frank and Kasper phases. Measurements of electronic specific heat seem to show indeed values of γ similar for those two types of phases, but somewhat too large compared with a free electrons model [29].

E. Resonant (d) states of solute transitional elements in normal (sp) metals and compounds.

In this family, two experimental data related to energetics are generally known:

1. Hume Rothery–Jones rules seem to be followed; but the transitional elements seem to act as if their d shells were absorbing a number of valence electrons, thus resulting in effective negative valencies: about 1 for Copper base alloys [4] and 2 for Aluminium base alloys [30].
2. The inclusion of transitional elements seem to stabilize somewhat these Hume Rothery–Jones phases.

There is extensive literature on these points for more or less classical crystal phases. Recent works have merely shown that quasicrystals and related Frank Kasper phases also follow these rules [31].

(a) Difficulties of the energetics results

These results are *a priori* surprising, for the following reasons, to be detailed elsewhere [32].

When transitional impurities are dissolved in a normal sp matrix, their d states, with energy E_d mix with the broad sp band into a virtual bound level which is progressively filled with d electrons in a transitional series [9]. For non-magnetic impurities, there is a single such state per atom, of degeneracy 10, with a maximum scattering at Fermi level when half filled. The maximum residual resistivity observed in Al T solid solutions arises when T is Cr or Mn, showing that these elements have approximate configurations of the type $(3d)_n(4sp)_{1.5}$

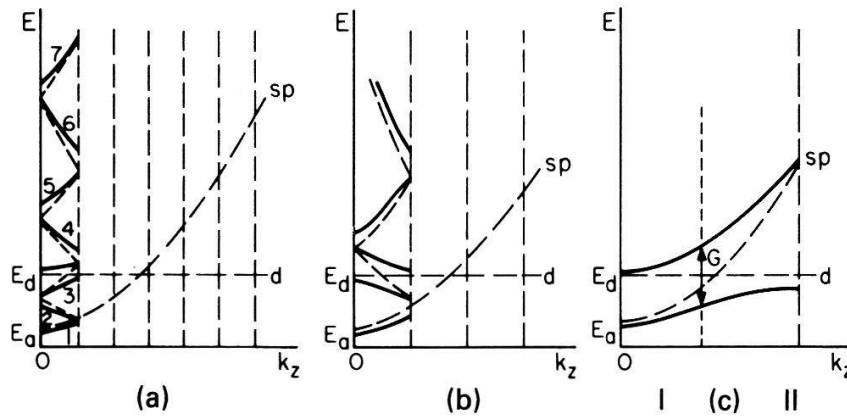


Figure 9

Mixture of d states and of a broad sp band for crystals of increasing concentration of transitional element. In punctuated lines, the bands to be coupled.

with $n \approx 4.5$ and 5.5 for Cr and Mn, respectively [39]. This is far from the configurations $(3d)_n$ with $n' \approx 8$ and 9 for Cr and Mn assumed by the Hume Rothery–Jones law [29]. A similar analysis can be made for Cu T with same conclusions.

Furthermore the Anderson model [34] developed for isolated transitional impurities can be extended to finite concentrations [35]. Although only qualitative, because it neglects the degeneracy of d states, it leads to but small energetic effects in general.

For crystals, it leads to the mixing in reciprocal space of a flat d band with a broad sp band (Fig. 9a, b, c). The density of states starts from a hump of Lorentzian shape at small concentrations, as expected for non-interacting impurities; for increasing concentrations, a gap of increasing width is produced near the center of the hump, which however keeps its Lorentzian wings (Fig. 11a, b, c). Quasicrystals, with a few bright Laue spots, are in this respect similar to large concentration crystals.

For random solute transitional elements, long range interferences due to multiple resonant scattering produce a secondary minimum in $n_d(E)$ which grows with concentration and can be approximately studied in a coherent potential type of approximation. This secondary minimum grows into a small (pseudo)-gap at

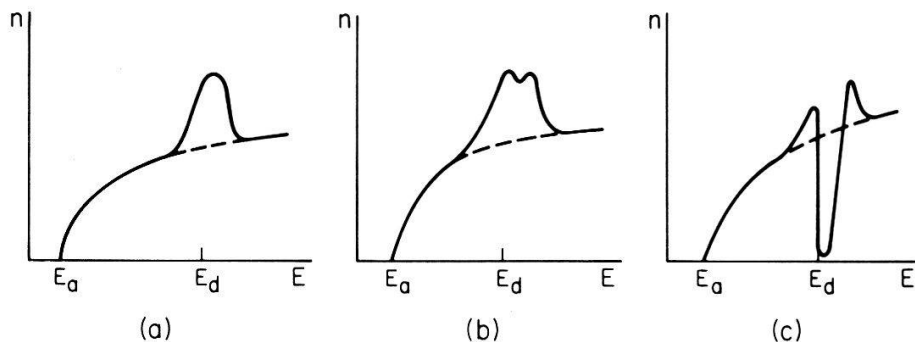


Figure 10

Random solid solutions of transitional elements in a normal metal: a, b, c for increasing concentrations. In punctuated lines, the CPA approximation.

very large concentrations [36], where, however, direct short range interactions should also be considered. Again these changes do not affect the long range Lorentzian wings of the density of d states (Fig. 10a, b, c).

It is then clear that, when dissolved in a normal metal, a transitional atom gains some energy, due to the broadening of its d shell. But this energy $2 \int^{E_M} n_d(E - E_d) dE$ is dominated by the contribution of the Lorentzian wing: it should not be very sensitive to concentration or long range ordering, which only affect the core of the Lorentzian. Furthermore this term is smaller than its equivalent when the transitional atom is included in a transitional matrix, where n_d has a much larger width.

Indeed the maximum stabilizing effect for cases considered so far are in the crystal or quasicrystal cases, with large concentration, when the Fermi level falls within the gap. This requires a specific number of d electrons, fixed by the fact that the ratio of d states below and above the gap is given by the ratio of volumes I and II, Fig. 9c. Now all perturbations in the core of the Lorentzian are of order of the gap energy, i.e.,

$$g = \frac{N |v|^2}{E_d - E_a} \approx \frac{2}{3\pi} \frac{c}{p} \pi n_0 |v|^2 \quad (12)$$

where c is the atomic concentration, p the valency of the matrix and $\pi n_0 |v|^2$ the width of the Lorentzian (n_0 density of sp states, v coupling matrix element between sp and d states). The maximum energy gained by the opening of the gap should then be of order

$$\delta E \approx 2Ng^2 n_d(E_d) = 2Ng^2 / \pi n_0 |v|^2.$$

or

$$\frac{1}{N} \delta E \approx \frac{8}{g\pi^3 p^2} \Delta_0^2 c^2. \quad (13)$$

As the width $\Delta_0 = \pi n_0 |v|^2$ is of the order of 1 eV, this energy is very small, especially in Al base alloys where $p \approx 3$.

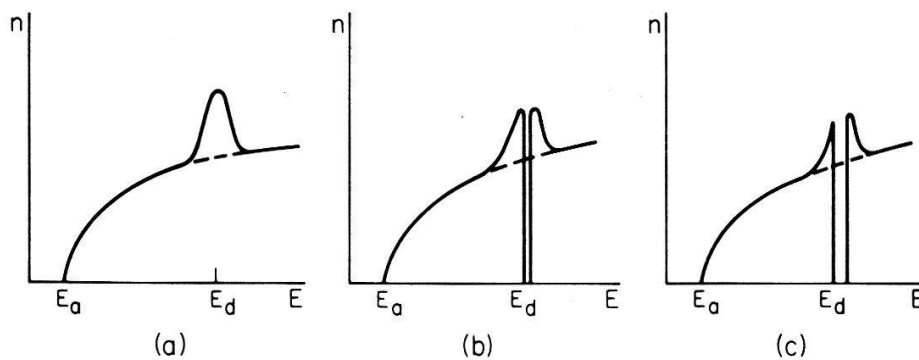


Figure 11
Crystals with transitional solute elements in normal matrices: a, b, c for increasing concentrations.

(b) Possible extension of Hume Rothery–Jones law for resonant scattering

There is a *special* case that was not considered in the discussion of Fig. 9. It corresponds indeed roughly to a Hume Rothery–Jones condition. It is when the flat band E_d interacts strongly with two broad bands E_1 and E_2 (Fig. 12).

If the flat band meets E_1 and E_2 at a Brillouin zone boundary, the local gap G_d will be twice as large as the corresponding local gap G at the crossing of E_d and E_1 , Fig. 9c. But, for half filled d levels, only half the d electrons will be in the lower band and affected by the gap opening, while half will be kept in the flat band. These two factors essentially compensate each other, leading to no special stability for the case of Fig. 12a.

The situation becomes different if we take into account that the broad sp band is not a free electron band but a nearly free electron band. The coherent scattering of the sp electrons by the atoms of the alloy (both matrix and solute elements) usually leads to a gap G_{sp} at the Brillouin zone boundary. Resonance of the broad sp band with the flat d band increases the gap to (Fig. 12b).

$$G = \sqrt{G_d^2 + G_{sp}^2} > G_d. \quad (14)$$

By interference with the preexisting sp gap, the d electrons now gain an energy $G - G_d$ with respect to the previous case. This is sizeable, as G_d and G_{sp} are both of order of 1 eV. Indeed

$$G_d 2\sqrt{N} |v| = 2 \left[\frac{2}{3\pi p} c(E_d - E_a) \Delta_0 \right]^{1/2} \quad (15)$$

where, for $\text{Al}_{80}\text{Mn}_{20}$, $c = 0.20$, $p = 2.5$ and $E_d - E_a = 10$ eV while $\Delta_0 = 1$ eV.

The optimum situation will occur when the condition described in Fig. 12 happens on the largest number of directions k_z in reciprocal space. This is roughly obtained when the angle θ of those k_z directions with the normal to the Brillouin zone boundary is maximum. From Fig. 12c, one sees that *the Brillouin zone is just inscribed in the Fermi sphere*.

This condition is be contrasted with the usual Hume Rothery–Jones condition described in A, where the Fermi sphere just touches the Brillouin zone

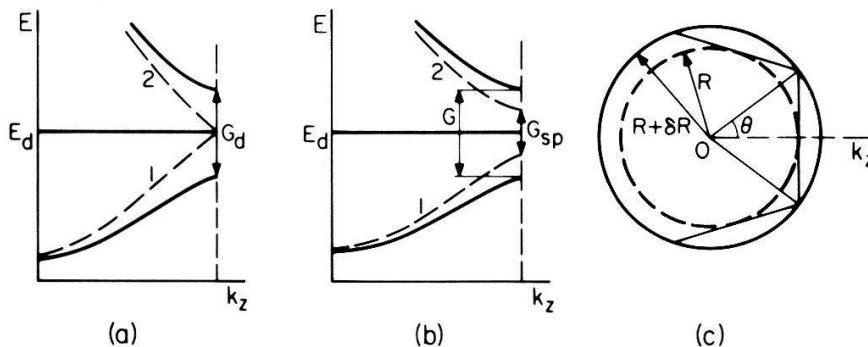


Figure 12
Hume Rothery–Jones condition for resonant scattering. (a) Free electron sp band; (b) nearly free electrons sp band; (c) condition in reciprocal space.

boundaries (Fig. 1). From the discussion in A and Fig. 2, one also sees that *the total stability is larger than the one expected merely from the sp gap.*

Because the new condition involves, for the same lattice geometry, a larger sphere, it requires a larger valence electron per atom ratio than the usual condition. As a result, if one insists in using the usual condition, one is lead to assume for the transitional elements a smaller valence electron per atom ratio, thus a smaller or even negative valency.

It is also clear that this discussion applies to quasicrystals as well as to crystal phases.

Consider for instance the $\text{Al}_{80}\text{Mn}_{20}$ quasicrystal phase [30]. Let n be the effective (negative) valency to be attributed to Mn in the usual Hume Rothery–Jones condition. The real (*sp*) valency is about 1.5. Then

$$\frac{0.8 \times 3 + 0.2 \times n}{0.8 \times 3 + 0.2 \times 1.5} = 1 - \frac{3\delta R}{R} \quad (16)$$

if RV and $R + \delta R$ are the radii of the two spheres of Fig. 12c. It is easy to see that

$$\frac{3\delta R}{R} \approx \frac{6}{\mu}. \quad (17)$$

Thus

$$n = 1.5 - \frac{81}{\mu} \quad (18)$$

This is indeed of order -2 if $\mu = 20$.

Equations similar to (16) for matrices of smaller valencies would lead, for similar degeneracies, to less negative effective valencies of transitional metals. This is indeed stated for Cu, Ag or Cu base alloys.

Nothing better than an order of magnitude agreement can be expected from this type of model. One should also stress that the magnetic effects observed in AlMn quasicrystals (but not in related Frank and Kasper phases) have not been discussed here, as they should lead only to small corrections.

F. Narrow d bands of transitional compounds

Here, the narrow but degenerate d band dominates the stability and most physical properties. It can be validly analyzed in the approximation of linear combination of atomic (d) orbitals [37], with eventual admixture of a broad sp band [37].

In its simplest d form, the density $n_d(E)$ gives rise to a change of energy per atom, with reference to the gaseous state, which can be given as a development of successive powers of U and J , the average intra-atomic Coulomb and exchange interactions between d electrons. For non-magnetic alloys, this reads for $z_d \leq 5$

[39]

$$E_d - E_d^a \approx E_B + \frac{z_d}{2} \left(1 - \frac{z_d}{10}\right) U + \frac{z_d}{2} (z_d - 1) J - 45 \frac{U^2}{w} \left[\frac{z_d}{10} \left(1 - \frac{z_d}{10}\right) \right]^2 + \frac{1}{2} q R \quad (19)$$

where

$$E_B = \frac{1}{N} 2 \int^{E_M} n_d(E - E_d) dE \quad (20)$$

$$z_d = \frac{1}{N} 2 \int^{E_M} n_d dE \quad (21)$$

and a similar expression for $z_d \geq 5$ where z_d is replaced by $10 - z_d$. R is a short range pair repulsion, w an estimate of the band width and q the number of neighbors.

We can use the well-known relation [40] then valid for the moments of n_d :

$$M_l = \int n_d(E - E_d)^l dE = S_l t^l \quad (22)$$

where t is an average transfer integral and S_l the number of closed loops of l interatomic jumps between neighboring atoms.

Fitting first a constant density n_d with a width w to the three first moments of the real $n_d(E)$ gives [39]

$$E_B \approx -\frac{z_d}{2} \left(1 - \frac{z_d}{10}\right) w \quad (23)$$

with

$$w \approx (12q)^{1/2} |t|. \quad (24)$$

This predicts that the most stable phases are closepacked and that their cohesive energy per atom varies qualitatively in the way schematized in Fig. 13. Within this limit, one can already understand why quasicrystals and related Frank and Kasper phases have stabilities comparable to those of the FCC or HCP phases: they have definitely larger values of q , but at the expense of some distortions of interatomic

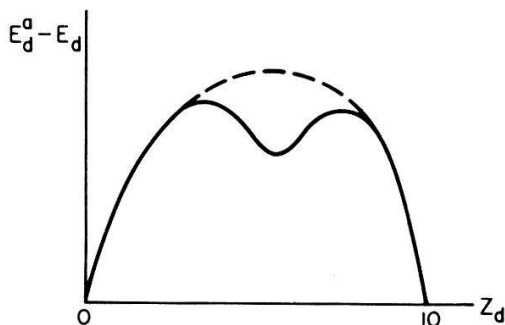


Figure 13
Cohesive energy $-(E_d - E_d^a)$ of transitional metals and compounds across a transitional series.

distances which increase the positive contribution of R in (19). The situation is somewhat analogous to that of the BCC phases, which is very closepacked with 14 nearest and next nearest neighbors, but at the expense of some differences in distances. Here again, one knows that the stability is comparable to that for the FCC or HCP phases.

To discuss the relative stability of these phases, one must go beyond the second moment, and at least up to M_4 . Indeed there is a regular succession of simple phases observed for pure metals and their binary alloys in the transitional series which was first stressed by Hume Rothery [4]. As expected from the symmetrical character of this series (FCC, HCP, BCC, HCP, FCC), M_3 plays no role here, as it has the same value for these different phases; but corrections associated with different values of M_4/M_2^2 and therefore with the relative weight of the tails of the d band, can explain this succession; and these conclusions are confirmed and made more quantitative when one considers further moments [41, 42].

A similar analysis has not yet been made for the Frank and Kasper phases (except for the special A_{15} [43] or Laves [44] phases), or *a fortiori* for quasicrystals (except for a cluster work) [45]. It is, however, interesting to note that a similar regularity is observed for those phases with small size and electronegativity effects: they are systematically observed for average d electrons per atom ratio that is somewhat on the right of the middle of the transitional series, between the BCC and HCP phases [46]. This suggests the same type of explanation.

First one can make a point that the Frank and Kasper phases, being based on imperfect tetragonal packing, are non alternate structures, with sizeable M_3 's, nearly comparable to those of the simple FCC, HCP and BCC phases, but *probably smaller*. Indeed, the atom at the center of an isohedron contributes to M_3 slightly more than the average for these simple phases (in the ratio 5/4); but there are many atoms with less perfect packing in real phases, thus an average M_3 will be below this upper limit.

Then Frank and Kasper phases have different atomic sites with very different numbers of neighbors q . M_2 is proportional to the average value of q , while M_4 depends more on a local average of q^2 . As a result, M_4/M_2^2 is expected to be larger in Frank and Kasper phases than in the close packed FCC or HCP phases, without reaching however the very large value of M_4/M_2^2 of the BCC phase.

It is therefore reasonable to expect that in the Frank and Kasper phases $n_d(E)$ has an asymmetry less marked than in the simpler phases and a relative weight of the tails intermediary between those of the FCC and HCP and of the BCC phases. Taking into account that, from (20) and (21)

$$\frac{d^2 E_B}{dz_d^2} = - \frac{1}{2n_d(E_M)} \quad (25)$$

one sees that $E_B(z_d)$ is likely to be less asymmetrical than for the simpler phases, and with a peaking near the middle of the series intermediary between BCC and

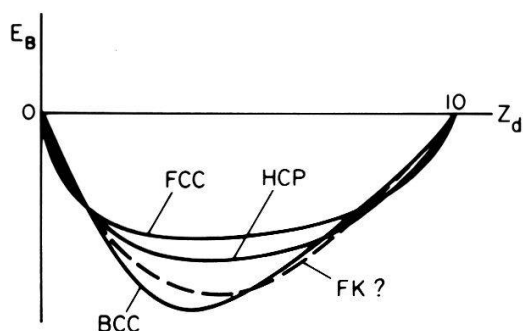


Figure 14
Expected variation of $E_B(z_d)$ for simple and Frank and Kasper (or quasicrystal) transitional phases.

HCP (Fig. 14) This would be coherent with observation for the Frank and Kasper phases as well as for the related quasicrystals where a similar discussion probably holds – computations reported in [43] to [45] are in qualitative agreement with this conclusion.

Conclusions

The quasicrystals and associated Frank and Kasper phase seem to follow the general rules of relative stability expressed initially by Hume Rothery for simpler crystal phases.

In ‘normal’ metals, a special stability is associated with the Fermi sphere of valence electrons just touching a set of Brillouin zone limits with strong intensity.

When acting as solute elements in normal metals, a similar rule applies where the d electrons are excluded from the count of valence electrons. For large enough concentrations of transitional solute elements, we propose that the maximum stability occurs when the Brillouin zone is just inscribed in the Fermi sphere. This would explain the apparent negative valences of these elements when the usual Hume Rothery–Jones condition is applied instead.

Transitional compounds lead to specific closely but unequally packed phases, with special stability near to but on the right of the middle of the transitional series.

Some general justifications can be offered for these rules, due to the ‘valency’ factor, which predominates when the two other Hume Rothery factors (size and electronegativity) are small. These justifications differ somewhat in the three cases considered. Furthermore, in each case, they result from an analysis of the coherent scattering or propagation of the valence electrons which can be expressed in terms of additive pair interactions only in the case of normal metals. Even in that case, the long range oscillations of these interactions have little relation to the simpler pair interactions often used in this field.

Appendix A. Interaction between two impurities in a free electron gas, in second order perturbation

Within the Born–Oppenheimer approximation, the energy of interaction $W(R_{ij})$ of two impurities at distance R_{ij} from each other is equal to the work done

by external forces to bring impurity j from infinity to R_{ij} . This in turn is equal to the change of electrostatic potential energy of the inner ion j .

This electrostatic energy can be split into four energies of interaction:

- with the free electrons,
- with the screening of the ion j considered when isolated,
- with impurity i , screened as if j did not exist,
- with the change in the two screenings due to interference effects at finite R_{ij} .

The two first terms do not vary with R_{ij}

The third is the term $V_j p_j^0$ used in the text.

The fourth is a term of order three in V , thus negligible to second order in perturbation.

The analysis still holds if, as for the interactions between say Mn and Al, one of the impurities has a strong potential.

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