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► **To cite this version:**

H. Jones. Concentrated solid solutions of normal metals. J. Phys. Radium, 1962, 23 (10), pp.637-639.
10.1051/jphysrad:019620023010063700 . jpa-00236652

HAL Id: jpa-00236652

<https://hal.archives-ouvertes.fr/jpa-00236652>

Submitted on 1 Jan 1962

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CONCENTRATED SOLID SOLUTIONS OF NORMAL METALS

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Résumé. — La théorie des diagrammes de phase relatifs aux alliages binaires est examinée à la lumière de travaux récents sur la surface de Fermi des métaux nobles. On étudie la relation entre les diagrammes énergie libre/composition et la densité de niveaux, et on revient sur l'explication des règles de Hume-Rothery. On discute les propriétés de la surface de Fermi du cuivre près du centre des faces hexagonales de la zone de Brillouin, la nature de la singularité de la densité de niveaux au point de contact, et la possibilité de réconcilier l'existence d'un contact avec les chaleurs spécifiques expérimentales des alliages de cuivre.

Abstract. — The theory of phase boundaries in binary alloys is reviewed in the light of modern work on the nature of the Fermi surfaces in the noble metals. Features of the free-energy-composition curves are investigated in relation to the density of electronic states, and the older interpretation of the Hume-Rothery rules is reexamined. General properties of the Fermi surface in the neighbourhood of the centre of the hexagonal faces of the Brillouin zone in copper, and the nature of the singularity in the density of states function at the point of contact are considered. The way in which the electronic specific heats of copper based alloys can be reconciled with a contacting Fermi surface in pure copper is discussed.

The theory of phase boundaries in alloys based on the noble metals was reviewed some four years ago by Cohen and Heine [1] in the light of the new knowledge of the Fermi surface revealed by experiments on the anomalous skin effect and the de Haas van Alphen effect. In particular they considered the interpretation of the Hume-Rothery rules taking into account the fact that in the pure noble metals the Fermi surface already touches the zone boundaries. In this introductory lecture I propose to touch on three matters: First to reconsider the theoretical basis of the Hume-Rothery rules, secondly to note a curious feature of the singularity in the density of states curve in face-centred cubic metals which may have relevance for the observed electronic specific heats, and, thirdly, to raise the question of the effect which statistical fluctuations in concentration can have on the electronic properties of such alloys as copper-nickel.

(i) Since the time of Gibbs it has been known that phase boundaries are determined by the behaviour of the free energy as a function of composition. In some cases the variation of phase boundaries with temperature can be exceedingly complicated particularly in the neighbourhood of the α/β transformation. Neglecting such complication the stability of phases at zero temperature can be discussed by replacing the free energy by the internal energy. In general a phase boundary occurs when the internal energy of the phase, regarded as a function of the composition, begins to rise sharply relative to the energy of a neighbouring phase. It is only the relative energies of the different crystal structures which are significant. A uniform change of energy throughout the whole

range of composition does not affect the positions of the boundaries. For this reason, in any electron theory, it is convenient to compare the total valency-electron energy with some standard state. The most convenient is that of a free electron gas of the same number density. In figure 1 curve (a)

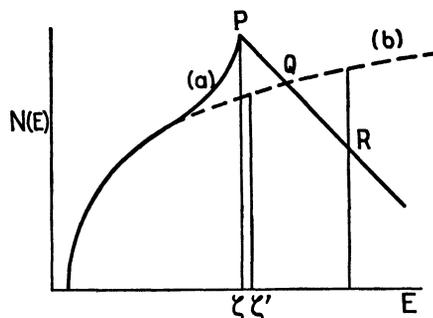


FIG. 1.

is taken to represent the density of electronic states in the metal and (b) in the free electron gas. If n denotes the number density let $U(n)$ be the internal energy of the metal and $U_0(n)$ that of the free electron gas, and let $\Delta U = U(n) - U_0(n)$. If ζ denotes the energy of the Fermi level in the metal and ζ' in the free electron gas when, in each case, the number density is n then

$$\frac{d\Delta U}{dn} = \zeta - \zeta' \quad \text{and} \quad \frac{d^2\Delta U}{dn^2} = \frac{1}{N(\zeta)} - \frac{1}{N_0(\zeta')},$$

where $N(\zeta)$ is the density of states at the Fermi level in the metal and $N_0(\zeta')$ in the gas.

The total energy difference is therefore as shown in figure 2. At P clearly $\zeta' > \zeta$ and $N(\zeta) > N_0(\zeta')$

and therefore both first and second derivatives of ΔU are negative. Near Q , $N(\zeta) = N_0(\zeta')$ with ζ' still greater than ζ . Hence this is a point of inflection. At R the areas under the two curves are equal and $\zeta = \zeta'$ with $N(\zeta) < N_0(\zeta')$. This is

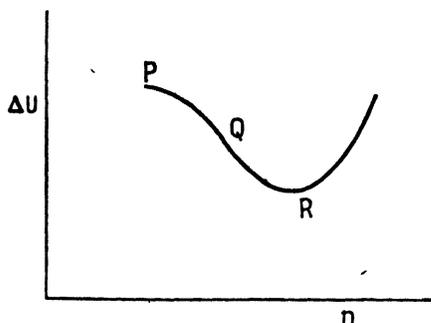


FIG. 2.

therefore the minimum and as can be seen will in general always lie well to the right of P . It would appear to make little difference to the position of the phase boundary whether the Fermi level in the pure metal is just before or just beyond the contact point P . What is important is that $N(E)$ should continue to fall up to the phase boundary. In copper-zinc, for example, up to an electron concentration of about 1.4 per atom.

(ii) The energy surfaces in the neighbourhood of contact with the zone boundaries show certain peculiarities in face-central cubic metals. It has long been known that the normal component of the gradient of the energy does not necessarily vanish over the hexagonal faces of the Brillouin zone. This is because there is no plane of reflection symmetry normal to the cubic axis. In every energy band the energy surfaces have 3-fold symmetry only about this axis. However, the line-contours formed by the intersections of the energy surfaces with the hexagonal plane faces have 6-fold symmetry about the centre. This is because the cubic group contains the inversion operator. If the hexagonal face is divided into six equilateral triangles, then at corresponding points of two neighbouring triangles the energies are equal but the gradients of the energy are of opposite signs.

Thus in a parallel plane just below the zone face only 3-fold symmetry exists. A model which shows the required symmetry can easily be conceived as follows (*): Imagine a sphere inside the Brillouin zone which does not touch the boundaries. Cut along the meridians (a), (b), (c) of figure 3, and displace the shaded segments relative to the unshaded until the surface just cuts the hexagonal faces. Finally transfer the caps to the opposite face on the inside of the zone, and round off sharp

(*) In this model only one pair of hexagonal faces is considered.

corners. Such a surface when cut by any plane parallel to the hexagonal face yields a finite cross-section, though not necessarily a cross-section having a stationary value. In fact, the surface although touching the zone boundaries may remain

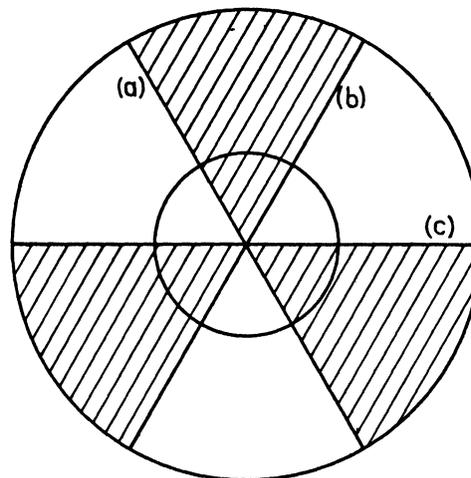


FIG. 3.

simply connected and its energy below the singularity of the density of states curve. To see this consider for example an alternative way of viewing this surface in relation to the Brillouin zone. As pointed out many years ago by Seitz one can visualize the zone as bounded by surfaces over which the normal component of the gradient of the energy vanishes. Instead of plane hexagonal faces there are fluted surfaces which bulge over 3 triangles and are indented over the other three. A possible Fermi surface would be one which would follow the form of the boundary without touching it but extending beyond the hexagonal planes at each face. Since this surface has not reached any point of vanishing ∇E it must lie to the left of the density peak. On the other hand as in the former representation it gives rise to a finite cross-section when cut by a plane normal to the cubic axis. It would thus appear that in face-centred cubic structures the contacting of energy surfaces with plane hexagonal zone boundaries and the occurrence of multiple connectivity are not necessarily the same events.

It is not perhaps impossible that this situation has some relevance to the observed electronic specific heats of the α -brasses which according to the observations of Rayne [2] show an initial rise with increasing electron concentration.

(iii) The third point I wish to raise is to what extent a disordered alloy can be regarded as a homogeneous system from the point of view of its electronic properties. In other words do statistical fluctuations in concentration play a significant part.

The effect is most likely to be noticeable when one component of the alloy is a transition metal e.g. Cu-Ni or Ag-Pd. Consider an alloy containing 20 per cent. of a transition metal. Take a region of 20 lattice sites in which therefore there would be on the average 4 transition metal atoms. What is the probability that there would be eight? Poisson's formula gives $4^8 e^{-4}/8! = .03$. Since 8 atoms in 20 corresponds to 40 per cent. this is the composition at which in bulk metal, the d-band

would begin to show vacancies. Would a region of 20 lattice sites be large enough to give an effect? There is perhaps here an analogy with the density of electronic states in a liquid metal where disorder can cause states to appear below the level of the band of the ordered crystal. One effect of fluctuations in an alloy containing a transition metal might be to cause an excess electronic specific heat above what would be given by the average state of the alloy.

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- [1] COHEN (M. H.) and HEINE (V.), *Phil. Mag.*, 1958, sup. vol. 7, 395. [2] RAYNE (J. A.), *Phys. Rev.*, 1957, 108, 22.
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