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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 48 e^{-4}/81 == .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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THE RIGID-BAND MODEL

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Abstract. — The present status of the rigid-band model of an alloy is reviewed with particular reference to the work of Cohen and Heine. A short account is also given of a recent attempt to obtain more quantitative information about the distortion of energy surfaces on alloying, by a direct calculation using the tight-binding approximation with a lattice of square potential wells.

1. Introduction. — The rigid-band model of an alloy assumes that the energy surfaces and density of states curve of the solvent metal remain unchanged on alloying, the only effect of the addition of the solute metal being, if its valency is greater than that of the solvent, to add electrons to the band, so swelling the Fermi surface and filling the density of states curve to a higher energy.

When it was thought that the Fermi surfaces in the noble metals were nearly spherical, this model provided a simple explanation of the Hume-Rothery rules, for a sphere which just touches the zone boundary of a face-centred cubic metal contains 1.36 electrons per atom. A peak would thus occur in the density of states curve at an electron to atom (e/a) ratio of about 1.36, which coincides approximately with the solubility limit of the α-phases of a large number of alloys of the noble metals with metals of higher valency. Similar considerations apply to the β- and γ-phase boundaries.

The demonstration by Pippard (1957) that the Fermi surface in pure copper is already in contact with the zone boundary (and Schoenberg (1960) has since shown that this is so in silver and gold also) destroys this simple theory based on spherical energy surfaces. However, it does not of itself invalidate the rigid-band model or the explanation of the Hume-Rothery rules thereby. In his original paper, Jones (1937) found that the peak of the density of states [N(E)] curve for copper occurred at an e/a ratio of 1.04 — that is to say, he found that the Fermi surface in pure copper must just about touch the zone boundary. None the less, his calculations showed that the α-phase boundary of Cu Zn, for example, should occur at an e/a ratio of about 1.4, in agreement with experiment. The phase boundary clearly depends upon the relative energies of the α- and β-phases, and does not occur immediately at the peak of the N(E) curve of the α-phase. The similar phase boundaries found in alloys of Cu, Ag and Au may be due simply
to a similarity in the energy band structures of
these metals.
Hume-Rothery and Roafe (1961) have suggested
that the $\alpha$-phase boundary is associated with a
second peak in the $N(E)$ curve, where contact is
made with the square faces of the zone. This may
indeed be true, but it is not necessary in order to
preserve the rigid-band model.
Perhaps more serious from the point of view of
the rigid-band model are the experimental values
of the electronic specific heats of Cu Zn and Cu Ge
obtained by Rayne (1957, 1958). If, as Pippard
has shown, the Fermi level is just beyond the first
peak in the $N(E)$ curve for pure Cu, we should
expect the density of states at the Fermi surface,
and consequently the electronic specific heat, to
fall as the $e/a$ ratio increases. Instead of this,
Rayne's results show that the electronic specific
heat rises and, in the case of Cu Zn at least, appar-
ently has a peak in the neighbourhood of
$e/a = 1.1$.

2. The Theory of Cohen and Heine. — In an
try to explain these results of Rayne, and also
to retain the simple explanation of the Hume-
Rothery rules based upon spherical energy surfaces,
Cohen and Heine (1958) suggested that the rigid-
band model be abandoned. They claimed that, on
adding an impurity to Cu, the Fermi surface, which
cuts the zone boundary in pure Cu, becomes more
spherical, that is to say, makes less contact with
the zone boundary, and may, in fact, pull away
from contact altogether in the neighbourhood of
$e/a = 1.1$. To offset this, we must take into
account the additional electrons contributed by a
polyvalent impurity, so that the Fermi surface
must swell, and hence, if contact is lost, it must be
re-established at a higher $e/a$ ratio.
The theory of Cohen and Heine is based upon
the size of the energy gap at the point of the zone
boundary closest to the centre of the zone — the
energy gap at the centre of a hexagonal zone face
in the case of the noble metals — and also upon the
relative energies of the states with $s$ and $p$ sym-
metries at this point.
In figure 1, $k$ is in the direction of the centre of a
hexagonal zone face (for the noble metals), $E_s$ and
$E_p$ are the energies of states with $s$ and $p$ sym-
metries at the zone boundary (the order of these may
be reversed), $E_0$ is the energy at the centre of the
zone, and $E_F$ is the Fermi level.
It is assumed that the parabolic energy curve
corresponding to spherical energy surfaces (with
effective mass not necessarily equal to $m$, however)
passes midway between $E_s$ and $E_p$ at the zone
face. If $E_p$ lies above the lower of $E_s$ and $E_p$, the
Fermi surface touches the zone face, otherwise not.
Using somewhat crude assumptions Cohen and
Heine relate the size of the energy gap to $\Delta_p$, the
difference between the $s$ and $p$ levels in a free
atom, which they obtain from experimental data.
Applying their method to the monovalent metals
they find that the Fermi surface in Li should touch
the zone boundary, which is not borne out by band
structure calculations, and that none of the Fermi
surfaces in the noble metals, although distorted
from spheres, should touch the zone boundary,
which disagrees with what is now known about
these metals. Little trust can thus be put in the
detailed results of Cohen and Heine, but this may
be due to the inadequacy of their approximations
rather than to an error of principle.
In discussing the $\alpha$-phase alloys of the noble
metals Cohen and Heine relate the energy gap to a
weighted average of $\Delta_p$ for the solute and solvent
metals. Since $(\Delta_{p\text{solvent}} > (\Delta_{p\text{solute}})$ for the alloys
considered, the average $\Delta_p$ is increased on alloying.
Cohen and Heine deduce that $E_p$ is always raised
relative to $E_s$ on alloying. In Cu, $E_p < E_s$, so that
the energy gap should decrease on alloying and the
energy surfaces become more spherical. This means
in turn that the peak in the $N(E)$ curve is moved to
a higher $e/a$ ratio. It was hoped that this would
explain the specific heat measurements of Rayne,
since the Fermi level might be moving up the ste-
dly descending part of the $N(E)$ curve as the peak
is displaced.
A detailed calculation by Ziman (1961), using an
approximate method similar to that of Jones (1937),
of the density of states in the noble metals, for
different values of the energy gap, shows, however,
that this is not the case. Figure 2 gives the results
of Ziman for a range of values of the quantity $u$,
which is proportional to the product of the energy
gap and $m^*$, the effective mass at the zone centre.
If we assume that there is little variation in $m^*$,
we see that, as the energy gap decreases, the density of states at the Fermi surface \((n = 1)\) falls. This is due to the fact that, although the peak in the \(N(E)\) curve moves to higher \(e/a\) ratios, the height of the peak decreases, presumably owing to an increase in the band width.

It should be noted that one could still get an increase in the electronic specific heat as the energy gap decreased if there was an increase in the value of \(u\) on alloying owing to a rapid increase in \(m^*\), but there is no reason to suppose that this is the case.

What the calculation of Ziman does show is that, if, as Cohen and Heine suggest, it is possible to base the band structure simply on the size of the energy gap, and this varies considerably on alloying, the rigid-band model is far from satisfactory.

3. A Quantitative Calculation using a Simplified Model. — Recently Mr. J. H. Tripp and I have been trying to find a simple model of an alloy which would permit a quantitative investigation of the theory of Cohen and Heine. So far we have not had any great success, and I shall briefly describe our results to date more with the hope of provoking useful comment than of making a significant contribution to the solution of the problem.

The first difficulty to be faced is that, not only is a rigorous solution impracticable, but the problem itself does not exist in a rigorous sense. In other words, to talk of the Fermi surface pulling away from the zone boundary in an alloy, or indeed to talk of energy surfaces at all in disordered alloys, involves an essentially approximate view of the situation. As soon as an impurity is introduced into a metal the strict periodicity of the lattice is lost. This means that the wave functions of the valence electrons, although they may still be extended, are no longer Bloch functions. The significance of the \(k\) vector is thus lost, and with it the strict significance of the energy surfaces and Brillouin zones. The density of states in energy retains its significance, of course.

It might be thought that perturbation theory at least would enable us to relate a one-electron state in the alloy with a state \(k\) in the pure metal, but it is not possible to do this in general, owing to the degeneracy of the states of the pure metal. If, indeed, the perturbing potential \(V\) introduced by the impurity is so small that first-order perturbation theory is appropriate, and we may ignore the off-diagonal matrix elements of \(V\), then it is certainly meaningful to talk of energy surfaces, at least as a good approximation. In this case the change in energy on alloying of a state \(\psi_k\) of the pure metal is given by

\[
\Delta E = \int \psi_k^* V \psi_k \ \mathrm{d}r.
\]

It may be noted that if the \(\psi_k\) were free-electron functions or Wigner-Seitz functions

\[
\psi_k(r) = e^{ik \cdot r} u_\alpha(r)
\]

this would lead immediately to the rigid-band model, for the energy of every state would be displaced by exactly the same amount; but this certainly cannot be true near the zone boundaries.

This first-order approximation is the one we have used in our calculation. As our initial model of the pure metal we considered a simple cubic lattice of square-well potentials, that is, spherical regions of constant potential surrounding each lattice point, and it was also assumed that nearest-neighbouring wells touch. In the alloy some of the wells were taken to be deeper or shallower as the case may be.

In the pure metal the wells were chosen sufficiently deep (taking the radius of a well to be 1 Å the depth was 57.1 eV) to give rise to two bound levels in an isolated well — a 1s level and a 2p level. The energy bands in the metal corresponding to these levels were calculated using tight-binding theory. The tight-binding wave functions were then used, in effect, to calculate by first-order perturbation theory the energy band structure of several alloys with various impurity well depths and concentrations.

Although we were principally interested in the lowest band, the \(s\) band, it was necessary to take

![Fig. 2. — Density of states in energy as a function of \(n\), the number of electrons per atom, calculated by Ziman (1961) for various values of the energy gap (\(\mu\approx\) energy gap \(\times\) effective mass).](image)
into account the interaction between the s and p bands in order to get a change in the energy surfaces on alloying. The energy surfaces of a band formed from s atomic functions only retain the same shape on alloying — only the band width changes.

The essential results for this initial model are shown in Table 1 and Figures 3 and 4. Unfortunately, it was not possible to isolate the impurity well depth from the concentration — the results depend only upon the value of the quantity $A$, where

$$A = \frac{(\text{Impurity well depth} - \text{Pure metal well depth})}{\text{Pure metal well depth}} \times \left(\frac{\text{No. of impurity atoms}}{\text{Total no. of atoms}}\right).$$

Thus, $A = -0.05$ corresponds to a range of alloys with shallower impurity wells, including one in which 5% of the wells have zero depth. On the other hand, $A = 0.05$ corresponds to a range of alloys with deeper impurity wells, including one in which 5% of the wells have twice the depth of the pure metal wells. It should be noted, in particular, that the results would be the same for a "virtual crystal", that is, a periodic lattice of wells whose depth is the weighted average of the pure metal and impurity well depths.

We have taken as a measure of the distortion of the energy surfaces from spheres the number of electrons per atom lying within the surface which touches the zone boundary. A sphere which touches the zone boundary contains 1.05 electrons per atom, whereas Table 1 shows that in our model of the pure metal ($A = 0$) the energy surface which touches the zone boundary contains only 0.478 electrons per atom. The energy surfaces are thus considerably distorted from spheres. However, we see that, when the impurity wells are shallower ($A = -0.05$) than the pure metal wells, the energy surfaces become more spherical — the surface which touches the zone boundary contains more electrons than in the pure metal. When the impurity wells are deeper ($A = 0.05$), the reverse is the case — the energy surfaces are more distorted from spheres. The smaller the energy gap the less spherical are the energy surfaces. This is contrary to the prediction of Chen and Heine for the noble metal alloy, but seems to be due to the use of square potential wells which touch.

The effect of the distortion of the energy surfaces is in any case very slight. Figure 3 shows the

<table>
<thead>
<tr>
<th>$A$</th>
<th>No. of electrons per atom in surface which touches zone</th>
<th>S-P Energy gap at centre of zone face (eV)</th>
<th>S band width (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.05</td>
<td>0.503</td>
<td>10.8</td>
<td>12.4</td>
</tr>
<tr>
<td>0</td>
<td>0.478</td>
<td>10.2</td>
<td>13.8</td>
</tr>
<tr>
<td>0.05</td>
<td>0.461</td>
<td>9.5</td>
<td>15.2</td>
</tr>
</tbody>
</table>

![Figure 3](image1.png)

**Fig. 3.** Density of states in energy as a function of $n$, the number of electrons per atom, for the lowest band.

![Figure 4](image2.png)

**Fig. 4.** Density of states in energy for the lowest band, when the band width is adjusted to be the same in each case.
density of states as a function of $n$, the number of electrons per atom, in the three cases considered. We note in passing that the density of states at the Fermi surface ($n = 1$ for the pure metal) increases as the energy gap increases but in view of what has been said above this is probably without significance. Figure 4 shows what the density of states curves become when the band width (the highest energy minus the lowest energy in the band) is taken to be the same in each case. We see that the effect on the density of states of the distortion of the energy surfaces is almost completely swamped by the change in the band width.

If any deduction can be made from the present calculation, therefore, it is that the change in the band width on alloying is probably more important, from the point of view of electronic specific heat calculations, than the distortion of the energy surfaces. This agrees with what can be deduced from the calculation of Ziman (1961).

Although I have only quoted the results for a simple cubic lattice, a similar calculation has almost been completed for a face-centred cubic lattice. However, much more consideration will have to be given to the approximations used, as well as to the many factors which have been ignored, before the significance of the results can be assessed.

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