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Charging and the Properties of Alloys

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In contrast to pure metals, the electron states in alloys exhibit a charging effect, i.e., a different electronic charge is deposited on each constituent in the alloy for a given state. The criterion for perturbation theory to be valid for an alloy is that the charging effect be small, i.e., the amplitude of an electron state be about the same on each constituent. It is not sufficient that the alloy be dilute. In fact if perturbation theory applies for a dilute alloy, it applies for any concentration. The charging effect is expected to be small, and thus perturbation theory to be valid, when the difference in the valence of the two constitutents is a small fraction of the smaller valence. The charging effect causes the energy of a given electron state in a binary alloy to deviate from a linear interpolation between the values of the pure metals. Such a linear interpolation is what one expects if the band structure is determined only by the average potential. Perturbation theory predicts that the specific heat of a binary solid-solution alloy deviates from a linear interpolation as $K\alpha(1\text{-}\alpha)$, where α is the fractional amount of one of the constituents and K depends, among other things, on the variation of the potential from the average and on the amount of short-range order in the alloy. Optical measurements at frequencies high compared with the relaxation time of the electrons measure the band structure determined by the average potential only. Experiments have shown that the properties of the Ag-Au alloy system *near the Fermi surface* can be treated by perturbation theory, and on this basis all of the experimental measurements of this alloy system can be understood, including recent specific-heat measurements. The d-band of the Ag-Au alloy system exhibits large charging effects and cannot be treated by perturbation theory.

I. INTRODUCTION

OUR understanding of the electronic properties of pure metals has shown such progress in recent years that it has been possible to get detailed information on the electronic properties which agrees rather well with theoretical calculations. It appears that we have a good physical understanding of the electronic structure of pure metals. The electronic structure of normal alloys is not in such a good quantitative state. There has recently been much theoretical work attempting to understand the electronic structure of alloys.[1–9] However, the experimental measurements to test these theories have not been as numerous as required. Recently, experimental measurements on the Ag-Au alloy system have shown a very simple behavior,[10] namely that the area of contact of the Fermi-surface neck with the Brillouin-zone boundaries varies linearly from pure silver to pure gold. This means that the shape of the Fermi surface in the Ag-Au alloys can be calculated from an average potential and that the properties of these alloys near the Fermi energy can be calculated by ordinary perturbation theory.[10] Thus we have in this system the first example in which it should be possible to expect quantitative agreement between theory and experiment for an alloy.

A detailed calculation of the properties of Ag-Au alloys should consist of first calculating the properties given by a periodic potential equal to the average potential, and then treating the difference between the average and actual potentials by perturbation theory. Since the potentials contributed by Ag and Au ions are rather well known, it should be possible to do such a calculation from first principles, as in the case of pure Ag and Au. We will not attempt such an ambitious plan in this paper, but we will use the data from some experiments to determine parameters with which other experimental properties can be calculated. The advantage of such an approach is that the mathematical details do not become too involved and it is possible to bring out the important physics involved.

There is one simple physical idea emphasized in this paper with which it is possible to understand various properties of the alloy both qualitatively and quantitatively. This is charging,[5] the difference in the amount of charge deposited by an electron in a given state on each constituent atom of the alloy. Charging is zero in pure metals but is most important in alloys. Among other effects, it modifies the potential of an ion from the value it has in the pure-metal case.[5] The next section will review the calculation of the properties of an alloy by perturbation theory and will show how charging determines when perturbation theory is applicable. In Sec. III we will derive in a simple manner Jones's theory of the effect of virtual scattering on the specific heat of

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alloys[4] directly from second-order perturbation theory. By this means it can be shown that this theory is not usually valid for dilute alloys. In this same section the optical properties and effects of short-range order on the electronic specific heat will be discussed. Section IV contains quantitative estimates of the expected electronic specific heat and charging effect in Ag-Au alloys and comparison with experiment. The conclusions are stated in Sec. V.

II. PERTURBATION THEORY

The perturbation theory of alloys has been described elsewhere by various people.[1,3] What will be given in this section is some physical insights into the cause of the energy shifts, and a discussion of when perturbation theory is applicable.

The model considered is a perfect lattice, occupied by two different constituents distributed in a random fashion, i.e., no long-range order present, though short-range order can be present. Thus we neglect lattice-distortion effects. It is also assumed that the ion cores of each constituent are stationary, centered on lattice points, and that their interactions with the conduction electrons can be represented by a potential. This potential may not be the same as the ion core has in the pure metal because of charging effects.[5] The potential of the alloy can be written as

$$V(\mathbf{r})=V_p(\mathbf{r})+V_s(\mathbf{r}),$$

where

$$V_p(\mathbf{r})=\sum\nolimits_{\mathbf{g}}[\alpha S(\mathbf{g})+(1-\alpha)G(\mathbf{g})]e^{i\mathbf{g}\cdot\mathbf{r}}$$

$$V_s(\mathbf{r})=\int V(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}d^3k. \tag{1}$$

Here $\mathbf{g}$ are the reciprocal vectors of the lattice; $S(\mathbf{g})$ and $G(\mathbf{g})$ are the $\mathbf{g}$th Fourier components of the potential from the type-1 and type-2 ions in the alloy, respectively; α is the atomic fraction of the type-1 atom in the alloy; and $V(\mathbf{k})$ is the $\mathbf{k}$th Fourier component of the alloy potential with the condition $V(\mathbf{g})=0$.

The zero-order wave functions are Bloch states determined by $V_p(\mathbf{r})$, the periodic part of $V(\mathbf{r})$. The energy of the alloy states to second order in $V_s(\mathbf{r})$ is given by[1]

$$E(\mathbf{k})=E_{\mathbf{k}}+E_1(\mathbf{k}),$$

where

$$E_1(\mathbf{k})=\sum\nolimits_{l}\frac{|(V_s)_{kl}|^2}{E_{\mathbf{k}}-E_{\mathbf{l}}}. \tag{2}$$

Here $(V_s)_{kl}$ is the matrix element of V_s between the Bloch states with wave vectors $\mathbf{k}$ and $\mathbf{l}$, and $E_{\mathbf{k}}$ is the energy of the zero-order Bloch states. The energies $E_{\mathbf{k}}$ are the same as for a pure metal with the periodic potential V_p. Such a pure metal has been called a "virtual crystal" and has a periodic potential at each lattice point which is just the average potential at a lattice point in the alloy. The $E(\mathbf{k})$ have a width which is also second order in V_s because of real scattering of the Bloch state $\mathbf{k}$ into other states of the same energy. We will delay the discussion of the importance of this real scattering until the next section. Throughout this paper the symbol $\sum$ denotes the principal value of the sum, which excludes the contribution from the states which contribute to real scattering.

From (1) and our previous discussion we see that

$$V_s(\mathbf{r})=\sum\nolimits_n\{V(\mathbf{r}-\mathbf{R}_n)-[\alpha V_1(\mathbf{r}-\mathbf{R}_n)+(1-\alpha)V_2(\mathbf{r}-\mathbf{R}_n)]\}, \tag{3}$$

where $\mathbf{R}_n$ are the positions of the lattice points; $V_1(\mathbf{r}-\mathbf{R}_n)$ and $V_2(\mathbf{r}-\mathbf{R}_n)$ are the ionic potentials of the type 1 and 2 atoms centered at $\mathbf{R}_n$, respectively; and $V(\mathbf{r}-\mathbf{R}_n)$ is the alloy potential centered at $\mathbf{R}_n$ which is V_1 or V_2 depending on which type of atom is centered at $\mathbf{R}_n$. Thus, $(V_s)_{lk}$ can be written as

$$\begin{aligned}(V_s)_{lk}&=((1-\alpha)/N)V_{12}(\mathbf{k},\mathbf{l})\sum\nolimits_a e^{i(\mathbf{k}-\mathbf{l})\cdot\mathbf{R}_a}\\&\quad-(\alpha/N)V_{12}(\mathbf{k},\mathbf{l})\sum\nolimits_s e^{i(\mathbf{k}-\mathbf{l})\cdot\mathbf{R}_s}\\&=\frac{V_{12}(\mathbf{k},\mathbf{l})}{N}\sum\nolimits_a e^{i(\mathbf{k}-\mathbf{l})\cdot\mathbf{R}_a},\end{aligned} \tag{4}$$

where

$$V_{12}(\mathbf{k},\mathbf{l})=\int_\Omega e^{i(\mathbf{k}-\mathbf{l})\cdot\mathbf{r}}U_{\mathbf{l}}^*(\mathbf{r})(V_1(\mathbf{r})-V_2(\mathbf{r}))U_{\mathbf{k}}(\mathbf{r})d^3r.$$

Here the integral for $V_{12}(\mathbf{k},\mathbf{l})$ is over a unit cell; the Bloch state is denoted by

$$\psi_{\mathbf{k}}=U_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}/\sqrt{N}, \tag{5}$$

where $U_{\mathbf{k}}(r)$ is normalized in a unit cell and has the periodicity of the lattice; $\mathbf{R}_a$ and $\mathbf{R}_s$ are the lattice points where the type-1 and type-2 atoms, respectively, are present; and in obtaining the last expression for $(V_s)_{lk}$ the relation

$$\sum\nolimits_a e^{i(\mathbf{k}-\mathbf{l})\cdot\mathbf{R}_a}+\sum\nolimits_s e^{i(\mathbf{k}-\mathbf{l})\cdot\mathbf{R}_s}=0 \tag{6}$$

is used.

Using the form for $(V_s)_{lk}$ given by (4), $E_1(\mathbf{k})$ of (2) becomes

$$E_1(\mathbf{k})=\frac{1}{N^2}\sum\nolimits_l\frac{|V_{12}(\mathbf{k},\mathbf{l})|^2G(\mathbf{k}-\mathbf{l})}{E_{\mathbf{k}}-E_{\mathbf{l}}}, \tag{7}$$

where

$$G(\mathbf{k}-\mathbf{l})=\sum\nolimits_a\sum\nolimits_b e^{i(\mathbf{k}-\mathbf{l})\cdot(\mathbf{R}_a-\mathbf{R}_b)}$$

and the double sum is over sites occupied by type-1 atoms. $G(\mathbf{k}-\mathbf{l})$ is the absolute square of the x-ray structure factor. Because $V_s(\mathbf{g})=0$, $V_{12}(\mathbf{k},\mathbf{l})=0$ when $\mathbf{k}-\mathbf{l}=\mathbf{g}$, and we need not consider $G(\mathbf{g})$. The subsequent forms for $G(\mathbf{k}-\mathbf{l})$ explicitly assume that $\mathbf{k}-\mathbf{l}\neq\mathbf{g}$.

We have assumed a particular distribution of the atoms in the alloy in order to calculate the above expression. Because of the very large number of atoms involved, the value of a physical quantity found by averaging over all possible distributions of the two constituents is representative of the alloy. The average of $E_1(\mathbf{k})$ over all possible distributions involves only $G(\mathbf{k}-\mathbf{l})$. After such averaging

$$\langle G(\mathbf{k}-\mathbf{l})\rangle_{\text{av}}=N_1\langle\textstyle\sum_a e^{i(\mathbf{k}-\mathbf{l})\cdot\mathbf{R}_a}\rangle_{\text{av}} \tag{8}$$

since all the lattice points $\mathbf{R}_b$ are equivalent and thus we can pick the lattice point $\mathbf{R}_b=0$. The angle brackets enclosing the expressions in (8) denote the required average, and N_1 is the total number of type-1 atoms in the alloy. From (6) one finds also that

$$\langle G(\mathbf{k}-\mathbf{l})\rangle_{\text{av}}=N_2\langle\textstyle\sum_s e^{i(\mathbf{k}-\mathbf{l})\cdot\mathbf{R}_s}\rangle_{\text{av}}, \tag{9}$$

where N_2 are the total number of type-2 atoms in the alloy.

Defining

$$\begin{aligned}S(\mathbf{k}-\mathbf{l})&=(N/N_2)\langle\textstyle\sum_a e^{i(\mathbf{k}-\mathbf{l})\cdot\mathbf{R}_a}\rangle_{\text{av}}\\&=(N/N_1)\langle\textstyle\sum_s e^{i(\mathbf{k}-\mathbf{l})\cdot\mathbf{R}_s}\rangle_{\text{av}},\end{aligned} \tag{10}$$

we can write

$$\langle G(\mathbf{k}-\mathbf{l})\rangle_{\text{av}}=N\alpha(1-\alpha)S(\mathbf{k}-\mathbf{l}), \tag{11}$$

where $N=N_1+N_2$, the total number of atoms in the alloy. Using (11) we can now write (7) as

$$E_1(\mathbf{k})=\frac{\alpha(1-\alpha)}{N}\sum_l\frac{|V_{12}(\mathbf{k},\mathbf{l})|^2S(\mathbf{k}-\mathbf{l})}{E_{\mathbf{k}}-E_{\mathbf{l}}}. \tag{12}$$

Since the periodic parts of the Bloch wave functions are normalized to one over a unit cell, $|V_{12}(\mathbf{k},\mathbf{l})|^2$ is of order one. It can be shown that $S(\mathbf{k}-\mathbf{l})$ is of order one, and thus $E_1(\mathbf{k})$ is of order $\alpha(1-\alpha)\langle|V_{12}|^2\rangle/\Delta$, where $\langle|V_{12}|^2\rangle$ is an average value of $|V_{12}(\mathbf{k},\mathbf{l})|^2$, and Δ is the width of the zero-order energy band. Regardless of the value of the ratio of $\langle|V_{12}|^2\rangle/\Delta^2$, when α is small enough $E_1(\mathbf{k})$ can be made a small fraction of Δ. This has led various investigators to assume that therefore perturbation theory is valid in very dilute alloys. That such is not the case has been pointed out by various other investigators.[6] What is required in order for perturbation theory to be valid is that the ratio $\langle|V_{12}|^2\rangle/\Delta^2$ be small, regardless of the value of α.

To understand this, it is instructive to introduce the concept of charging in an alloy and to calculate its value. In general, the electronic states in an alloy have different amplitudes in the vicinity of the different constituents. The different constituents in the alloy thus can become electrically charged with respect to one another, affecting the potential contributed by a given constituent in the alloy. Since the amount of charging also depends on the potential differences between the constituents, a self-consistent solution is required.[5] The potential that we are using in our discussion here is assumed to be the self-consistent one which includes all charging effects. Such charging effects are not present in pure metals because each atom is equivalent to every other one.

The wave function in the alloy to first order in V_s is given by

$$\Psi_{\mathbf{k}}=\Psi_{\mathbf{k}}+\textstyle\sum_{\mathbf{l}}(V_s)_{lk}\Psi_{\mathbf{l}}/(E_{\mathbf{k}}-E_{\mathbf{l}})). \tag{13}$$

The average amount of charge about the type-1 atom, $\rho_1(\mathbf{k})$, can be obtained by integrating the absolute square of Eq. (13) over the unit cell about the type-1 atom and averaging over such unit cells. Doing this we obtain

$$\rho_1(\mathbf{k})=\frac{1}{N}\left(1+\frac{2(1-\alpha)}{N}\operatorname{Re}\sum_{\mathbf{l}}\frac{V_{12}(\mathbf{k},\mathbf{l})\rho(\mathbf{k},\mathbf{l})S(\mathbf{k}-\mathbf{l})}{E_{\mathbf{k}}-E_{\mathbf{l}}}\right), \tag{14}$$

where

$$\rho(\mathbf{k},\mathbf{l})=\int_\Omega e^{i(\mathbf{l}-\mathbf{k})\cdot(\mathbf{r}-\mathbf{R}_a)}U_l(\mathbf{r})U_k^*(\mathbf{r})d^3r,$$

Re means to take the real part, and the integration is over the unit cell centered on $\mathbf{R}_a$. Similarly we find for the type-2 atoms

$$\rho_2(\mathbf{k})=\frac{1}{N}\left(1-\frac{2\alpha}{N}\operatorname{Re}\sum_l\frac{V_{12}(\mathbf{k},\mathbf{l})\rho(\mathbf{k},\mathbf{l})S(\mathbf{k}-\mathbf{l})}{E_{\mathbf{k}}-E_{\mathbf{l}}}\right). \tag{15}$$

Remembering that α is the fraction of type-1 atoms in the alloy, we see that even for dilute alloys [α or $1-\alpha$ very small], the fractional deviation from the average value of $1/N$ of the charging about the impurity atoms is of order $\langle V_{12}\rangle/\Delta$. In order for perturbation theory to be valid, this charge deviation must be small, and thus $\langle V_{12}\rangle/\Delta$ must be small regardless of the concentration of the alloy. In fact, if perturbation theory is valid for a dilute alloy, it will be even more valid for the same alloy at higher concentrations.

We now will show that the $E_1(\mathbf{k})$ calculated from perturbation theory is correctly calculated only when the charging effect is also correctly calculated from perturbation theory. We will prove an even stronger statement: whenever the charging can be calculated correctly, even when perturbation theory is not valid, the energy can also be calculated correctly. In fact the charging effect is the cause of the change in the value of the energy levels from $E_{\mathbf{k}}$. To show this we calculate $\int\psi_{\mathbf{k}}((\mathbf{r})V_s(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r})d^3r$ within the unit cell of a type-1 atom and add up the contributions of all such type-1 atoms. This is the contribution to the potential energy of the type-1 atoms. We do the corresponding calculation for the type-2 atoms. The sum of the contributions from the type-1 and type-2 atoms gives us $2E(\mathbf{k})$, which is what we expect from the virial theorem. The term $E_1(\mathbf{k})$ in (2), (7), and (12) comes from the charging effect. If the charging is zero, then $E_1(\mathbf{k})=0$. It is interesting to note that even in a very dilute alloy the impurities contribute the same order of magnitude to $E_1(\mathbf{k})$ as do the host atoms. This is because, although there are $N\alpha$ impurities, their charging effect from (15) is of the order of $(1-\alpha)/N$ and their total effect is of the order of $\alpha(1-\alpha)$. There are $N(1-\alpha)$ host atoms present, but the charging effect on them is only of the order of α/N and thus their contribution to $E_1(\mathbf{k})$ is also of order $\alpha(1-\alpha)$. Thus, the charging effect on both impurities and host have to be known to the same percentage accuracy, and if perturbation theory is not valid for the charging effect, it is not valid for the energy values either.

This relation between charging and the energy of a state in the alloy is simply the consequence of the virial theorem and thus is valid in all alloys where the interaction between the ions and the conduction electrons can be represented by a potential. This relation can be used to estimate the charging in an alloy by measuring the variation of the energy of a state with alloying. Consider an alloy which can be treated by the tight-binding approximation. Then the wave function in the vicinity of an atom is the same independent of the state. In this case the energy of a state is approximately given by

$$E(\alpha)=\alpha\rho_1E_1+(1-\alpha)\rho_2E_2\,, \tag{16}$$

where ρ_1 and ρ_2 are proportional to the charge deposited on each type-1 and type-2 atom, respectively, and satisfy the relation

$$\alpha\rho_1+(1-\alpha)\rho_2=1\,. \tag{17}$$

Using (17) we can write (16) as

$$E(\alpha)=E_1+(1-\alpha)\rho_2E_{21}\,, \tag{18}$$

where $E_{21}=E_2-E_1$.
If there were no charging then $\rho_1=\rho_2=1$ and (18) would become

$$E_0(\alpha)=E_1+(1-\alpha)E_{21}\,. \tag{19}$$

There is a linear variation in E_0 with concentration in this case. In the case when charging is present ρ_2 as is shown by (14) and (15), varies with α, and we find a nonlinear variation of E with α. From (18) and (19), ρ_2 is given by

$$(dE/d\alpha)/(dE_0/d\alpha)=\rho_2(\alpha)-(1-\alpha)d\rho_2/d\alpha\,. \tag{20}$$

In a similar fashion we obtain

$$(dE/d\alpha)/(dE_0/d\alpha)=\rho_1(\alpha)+\alpha d\rho_1/d\alpha\,. \tag{21}$$

We also have

$$\begin{aligned}\rho_2(\alpha)&=(E(\alpha)-E_1)/(E_0(\alpha)-E_1)\\ \rho_1(\alpha)&=(E(\alpha)-E_2)/(E_0(\alpha)-E_2)\\ \rho_2(\alpha)/\rho_1(\alpha)&=[(E(\alpha)-E_1)/(E(\alpha)-E_2)]\alpha/(\alpha-1))\,.\end{aligned} \tag{22}$$

Although (18) and (20)–(22) are probably more accurate for alloys in the tight-binding approximation, they still can be used for any alloy to give an estimate of the charging effect.

III. ALLOY PROPERTIES

We now proceed to calculate the specific heat of the alloy. To second order in perturbation theory the Bloch states have an energy given by (2) and a lifetime which is second order in V_s. This lifetime produces a width to the energy of the Bloch states which contributes a correction to the density of states of fourth order in V_s. We will be neglecting this order and can therefore neglect the lifetime effects on the specific heat. Therefore the density of states of the alloy, to second order in perturbation theory, can be calculated with the same expression as used for pure metals with $E(\mathbf{k})$ given by (2). We have then that the density of states per unit volume is given by

$$\rho(E)=\frac{1}{4\pi^3V}\int\frac{dS}{v}\,, \tag{23}$$

where

$$\hbar v=|\nabla_{\mathbf{k}}E(\mathbf{k})|\,,$$

V is the volume of the alloy, and the integral is over the constant-energy surface in $\mathbf{k}$ space, $E=E(\mathbf{k})$. We assume, following Jones,[4] that $E_1(\mathbf{k})$ of (2) depends only on $E_{\mathbf{k}}$. Then, using Eq. (2), Eq. (23) becomes

$$\rho(E(\mathbf{k}))=\rho_0(E_{\mathbf{k}})(1-\partial E_1/\partial E_{\mathbf{k}})\,, \tag{24}$$

where $\rho_0(E_{\mathbf{k}})$ is the zero-order density of states at $E_{\mathbf{k}}$. If the Fermi level in zero order is at $E_{\mathbf{k}}$, then in the alloy it will be at $E(\mathbf{k})$, and γ, the coefficient of the linear temperature term of the low-temperature specific heat, will be given by

$$\gamma=\gamma_0(1-\partial E_1/\partial E_{\mathbf{k}})\,, \tag{25}$$

since it is proportional to the density of states. Here γ_0 is the γ in zero order.

Jones[4] has also calculated on expression equivalent to (25). His corresponding equation is different from (25) since he is calculating something slightly different. Jones compares γ and γ_0 at the same energy, while we have compared them at the same $\mathbf{k}$. The assumption that $E_1(\mathbf{k})$ depends only on $E_{\mathbf{k}}$ means that the Fermi surface remains the same size and shape in zero and second order if the number of electrons per unit volume does not change. In that case, then, we have compared γ and γ_0 at the Fermi surface. The Fermi energy changes by the amount $E_1(\mathbf{k}_F)$, where $\mathbf{k}_F$ is the Fermi momentum, and if we add the change in γ produced by this shifting of $E(\mathbf{k})$ we obtain exactly the same expression as given by Jones. Jones has stated that (25) is valid for dilute alloys, but as we have shown in the previous section, this is incorrect. Equation (25) is valid only when perturbation theory is valid and then for all concentrations.

Using the expression for $E_1(\mathbf{k})$ given in (12) and changing the sum into an integral we can write (25) in the form

$$(\gamma-\gamma_0)/\gamma_0=K\alpha(1-\alpha)\,, \tag{26}$$

where

$$K=\frac{1}{(2\pi)^3N}\frac{\partial}{\partial E_{\mathbf{k}}}\int\frac{|V_{12}(\mathbf{k},\mathbf{l})|^2S(\mathbf{k}-\mathbf{l})}{E_{\mathbf{k}}-E_{\mathbf{l}}}d^3l\,. \tag{27}$$

In Eq. (26), only $S(\mathbf{k}-\mathbf{l})$ and $\alpha(1-\alpha)$ could depend on α. For a completely random alloy with no short-range order, $S(\mathbf{k}-\mathbf{l})=1$. When short-range order is nonzero, $S(\mathbf{k}-\mathbf{l})$ will depend on this short-range order, but if the short-range order parameters are independent of α, then $S(\mathbf{k}-\mathbf{l})$, and thus K, remains independent of α. The specific heat of alloys depends on short-range order through K.

In discussing the optical properties of alloys we can no longer neglect the finite lifetime of the Bloch states. This lifetime introduces an absorption mechanism for light. For example, in the case when $V_p=0$, the zero-order wave functions are free-electron states. For $V_s=0$ the optical absorption occurs only at zero frequency, but when $V_s\neq 0$, this absorption is spread out in frequencies about zero. An example of this phenomenon is the Drude theory of the optical constants with a finite relaxation time τ for the electrons. When the frequency of the light ω is much greater than τ, the optical constants are the same as the case for $\tau\rightarrow\infty$, or $V_s=0$. This follows directly from the sum rule for oscillator strengths. In an analogous fashion one expects that for $\omega\tau\gg 1$ the optical constants of an alloy with $V_p\neq 0$ and $V_s\neq 0$ will also be the same as those for the metal with the same V_p but $V_s=0$. If V_s is small compared with interband energies, it will not produce any appreciable mixing between bands, only scattering within the band. Then an analogy with the free-electron case should hold, and when $\omega\tau\gg 1$, but ω is less than interband frequencies, the properties of the band with $V_s=0$ should be seen.

Whereas according to perturbation theory the specific heat depends on both V_p and V_s, optical measurements, when $\omega\tau\gg 1$ and V_s is much less than interband energies, depend only on V_p and measure the same properties as the "virtual" pure metal determined by V_p alone. In other words, at high enough frequencies, V_s is not seen in optical measurements.

The alloy electron states to second order in perturbation theory have a dc transport relaxation time given by[11]

$$1/\tau_{\mathbf{k}}=\frac{\alpha(1-\alpha)V}{2\pi\hbar N}\int|V_{12}(\mathbf{k},\mathbf{l})|^2|\nabla_l E_l|^{-1}\times(1-\cos\theta)S(\mathbf{k}-\mathbf{l})dS_l, \qquad (28)$$

where $\tau_{\mathbf{k}}$ is the relaxation time of an electron state $\mathbf{k}$, and dS_l is an element of area in the Fermi surface at $\mathbf{l}$. Cylindrical symmetry in the scattering about $\mathbf{k}$ is assumed. The relaxation time, and thus the residual resistance, varies with concentration as $\alpha(1-\alpha)$. This result was first given by Nordheim.[12]

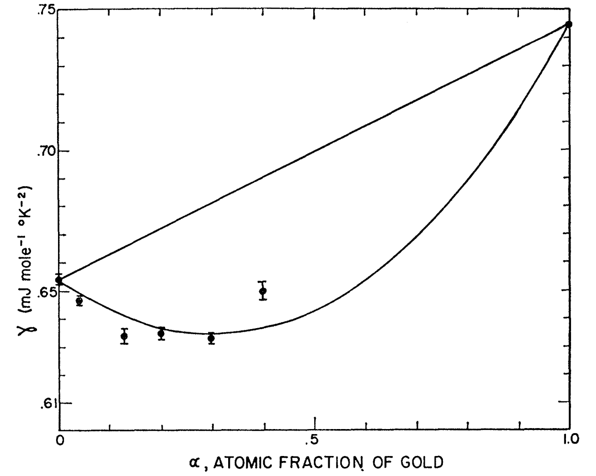

FIG. 1. The coefficient γ of the linear-temperature term in the low-temperature specific heat of Ag-Au alloys. The points are from the experiment of Ref. 13. The straight line is the zero-order value γ_0. The other curve is Eq. (26) with $K=-0.33$.

IV. Ag-Au ALLOYS

Since they may have small charging effects, Ag-Au alloys look like prime candidates for treatment by perturbation theory. The experimental evidence proves that this is the case.

The residual resistance of Ag-Au alloys[11] varies with composition in agreement with Nordheim's formula Eq. (28). Even stronger evidence comes from the recent optical measurements of the polar-reflection Faraday effect in Ag-Au alloys.[10] These have shown that the Fermi-surface neck contact with the Brillouin-zone boundaries linearly from pure silver to pure gold. This is what one expects from perturbation theory, as pointed out in the last section. We will show that recent specific-heat mesurements on Ag-Au alloys have the form given by (26) and are consistent with the resistance measurements. In addition, we will roughly estimate the charging effect.

Recent specific-heat measurements on Ag-Au alloys[13] have given the results plotted in Fig. 1. The zero-order γ_0 in (26) varies linearly between pure Ag and pure Au as shown in Fig. 1. The difference between the measured γ and γ_0 is consistent with the form in (26), as is shown in Fig. 1, where $(\gamma-\gamma_0)/\gamma_0=-0.33\,\alpha(1-\alpha)$ is plotted. An independent estimate of K in (26) can be obtained from measurements of the residual resistance ρ, by using (28), which depends on the same $|V_{12}(\mathbf{k},\mathbf{l})|^2$ as determine K. Table I gives the value of $\rho/\alpha(1-\alpha)$ determined from experimental data. From this, τ can be determined by $\rho=mV/Ne^2\tau$, where N/V, the number of electrons per unit volume, is given in the Table and the free-electron mass is used for m. Approximating the Fermi surface of Ag by a sphere, and assuming the

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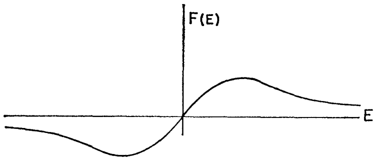

FIG. 2. The general form for $F(E)$ in Eq. (30) for a $\rho(E)$ symmetric about $E=0$.

$|V_{12}(\mathbf{k},\mathbf{l})|^2$ is a constant and that the electrons in Ag have the free-electron velocity at the Fermi surface, we obtain the value for $\langle|V_{12}|^2\rangle$ given in the table.

Neglecting any short-range-order effects, we can set $S(\mathbf{k}-\mathbf{l})=1$ in (27). Again assuming the $|V_{12}(\mathbf{k},\mathbf{l})|^2$ are a constant, we can write from (27)

$$-K=[\langle|V_{12}|^2\rangle/2N]\partial F(E)/\partial E\,, \tag{29}$$

where

$$F(E)=\int_{-\infty}^{\infty}\frac{\rho_s(\epsilon)d\epsilon}{E-\epsilon}\,.$$

Here $\rho_s(\epsilon)$ is the density of states corresponding to those states with s symmetry only. It is being assumed that all of the electrons at the Fermi surface in Ag or Au have s-like symmetry and that the potentials due to Ag and Au ions are spherically symmetric. Then $V_{12}(\mathbf{k},\mathbf{l})$ only couples to states $\mathbf{l}$ which have s symmetry. This is a simplification that is not strictly true, since it is known that the electron states near the necks in Ag and Au have p-like symmetry. However, most of the Fermi-surface states should be s-like. The important thing is that none of the states at the Fermi surface, with either p or s symmetry, couples via $V_{12}(\mathbf{k},\mathbf{l})$ to the d states below the Fermi surface. The importance of this is explained in the next paragraph.

According to band calculations by Segall,[14] $\rho_s(\epsilon)$ appears to have a shape symmetric about the middle. To estimate $F(E)$ we choose for $\rho(\epsilon)$ the form

$$\rho(\epsilon)=\tfrac{3}{2}(N/E_F)[1-(\epsilon/E_F)^2]\,, \tag{30}$$

where $2E_F$ is the total width of the band, and the Fermi level is at $\epsilon=0$. With this $\rho(\epsilon)$, the function $F(E)$ has the form shown in Fig. 2 and is given by

$$F(E)=\frac{3N}{2E_F}\left[(1-x^2)\ln\left|\frac{1+x}{1-x}\right|+2x\right], \tag{31}$$

where $x=E/E_F$. At the Fermi energy, $E=0$, $\partial F(E)/\partial E$ is positive and thus K is negative, in agreement with experiment. If the $V_{12}(\mathbf{k},\mathbf{l})$ had appreciable values between the states at the Fermi energy and the d band below, then this would give a positive contribution to K which would overwhelm the negative contribution from the s and p electrons and would destroy any agreement with experiment. As discussed in the previous paragraph, $V_{12}(\mathbf{k},\mathbf{l})$ to the d band should be negligible.

TABLE I. Values of parameters for Ag-Au alloys.

$\rho/\alpha(1-\alpha)$[a]	3.6×10^{-7} Ωm
$\langle1/\tau\rangle$	5.9×10^{12} sec^{-1}
N/V	5.9×10^{22}/cm^3
$\langle\|V_{12}\|^2\rangle$	1.2×10^{-24} ergs^2
E_F	8×10^{-12} ergs
K_{calc}	-0.05
K_{expt}	-0.33

[a] References 11 and 16.

Using the values of $\langle|V_{12}|^2\rangle$ and E_F in Table I we estimate K to have the value -0.05. This has the same sign as the experimental value but is about six times smaller. In view of the crudeness of the calculation that led to the numerical estimate for K, it may not be surprising that there is such a large discrepancy from the measured value. The portions of the numerical estimate that are weakest are the somewhat arbitrary assumption of $\rho(\epsilon)$ in (30) and a constant value for $|V_{12}(\mathbf{k},\mathbf{l})|^2$. One expects that $V_{12}(\mathbf{k},\mathbf{l})$ provides scattering that is peaked in the forward direction. This would then require a larger value for $\langle|V_{12}|^2\rangle$ to give the same value for $1/\tau$ in (29). The necessary amount of peaking in the forward direction to give agreement with experiment is not unreasonable. Such an effect would also make $\rho_s(\epsilon)$ in (29) effectively more peaked around the Fermi energy because $|V_{12}(\mathbf{k},\mathbf{l})|$ would then couple more strongly to the states closest to the Fermi energy. Such greater effective peaking in $\rho_s(\epsilon)$ would also increase the magnitude of K to give better agreement with experiment. In view of these uncertainties it is felt that the estimated and measured values of K are not in disagreement. Certainly, the sign of K is correctly predicted by the theory.

In the calculation of K we have not estimated or included the effects of short-range order and many-body effects. An estimate of the short-range order present in Ag-Au alloys indicate that it probably has a negligible effect on K.

Most authorities now believe that direct electron-electron interactions do not appreciably change the specific heat. In the case of the Ag-Au alloys, where the electron states are not much different from those of pure Ag and Au, the change in γ due to alloying should be a small percentage of the effect in the pure metals and thus should be negligible. The electron-phonon interaction can produce a large effect on γ. However, in Ag and Au there is evidence that the electron-phonon enhancement of γ is small from the close agreement between the band, optical, and specific-heat masses. In addition, the Debye temperature of the alloys deviates only about 5°K, out of a Debye temperature of about 200°K, from a linear interpolation between pure Ag and Au. Thus the deviation from linearity due to alloying should be a small fraction of the total phonon effect and is probably much less than 1% and negligible.

Finally, we estimate the charging expected using (14) and the same model as in estimating K. Equation (14) contains the new quantity $\rho(\mathbf{k},\mathbf{l})$. Again, a detailed calculation is required to accurately determine $\rho(\mathbf{k},\mathbf{l})$.

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[14] B. Segall, General Electric Research Laboratory Report No. RL-2785 G (unpublished).

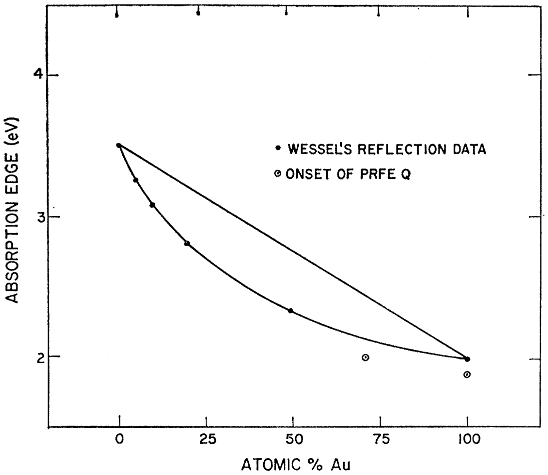

FIG. 3. The *d*-band optical-absorption-edge energy versus composition for the Ag-Au alloy system. The data are taken from Refs. 10 and 17.

A rough estimate can be obtained by assuming $U_1(\mathbf{r})$ is a constant; this gives $\rho(\mathbf{k},\mathbf{l})\approx 0.6$. Then about 0.2 of an electron charge is transferred between the silver and the gold. As Mott[15] points out, gold should have a more attractive potential, so that the Au ions have the greater electronic charge about them. This estimate is in agreement with the estimate of Roberts, Becher, Obenshain, and Thomson[16] who also measure that the *s*-type charge on Au varies linearly with α. Equations (14) and (15) are in agreement with this variation. The charging due to the *s* states is relatively small, e.g., for states at the Fermi surface in Ag-Au alloys it is much less than 0.2, since $F(E)$ is zero there; but the same is not true for the *d*-band states. We use the relation between charging and the energy variation of a given state with alloying given in (22) to estimate the charging in the *d* band of Ag-Au alloys. In Fig. 3 is plotted the energy of the initiation of the optical absorption in Ag-Au alloys based on the measurements of Refs. (10) and (17). This energy is the depth of the top of the *d*-band below the Fermi energy. Neglecting the variation of the Fermi energy itself, Fig. 3 then gives us $E(\alpha)$ in (22). Analysis of these data using (22) gives that

$$\rho_{\mathrm{Ag}}/\rho_{\mathrm{Au}}\approx 3.6 \qquad (32)$$

throughout the entire concentration range, i.e., the *d*-electron state at the top of the band deposits about 3.6 times the electronic charge on a Au ion that it does on a Ag ion. Clearly, this situation cannot be treated by perturbation theory. It has been shown[5] that when a band is filled, as in the case for the *d* band in Ag-Au alloys, there can be no net charging effect. Thus the greater charge deposited on the Au by the top *d*-band state has to be compensated by other states which deposit more charge on the Ag atoms. The behavior found in the *d* band of the Ag-Au alloy system is what is expected theoretically,[5] since the top of the *d* band of Au is closer to the Fermi surface than is that of Ag.

V. SUMMARY AND CONCLUSION

The exact wave function in a nonperiodic system is very complicated and for that reason is not very useful for obtaining a simple physical understanding of alloys. This paper points out that charging is a simple physical concept with which many alloy properties can be understood. Perturbation theory breaks down when the charging is large, and in the extreme case where the wave function has an amplitude on only one or the other constituent the band structure breaks up into two separate ones, each one depending on only the properties of one constituent.[2,5] In dilute alloys this corresponds to bound states being formed. The concept of charging makes it intuitively straightforward to pass from the bound-state to the perturbation-theory limit. In intermediate-type alloys the charging is large but there is appreciable amplitude on all constituents. In this paper it has been shown that charging is small when $\langle|V_{12}|\rangle/\Delta$ is small and vice versa. This is equivalent to the criterion found in the tight-binding approximation.[5]

The energies of the states in the alloy are directly understood in terms of charging. It has been shown that the energy change produced by the nonperiodic part of the potential is directly related to charging by the virial theorem. In fact a measurement of the variation of the energy of a given state as a function of alloying is the most direct way to measure charging in this state. Charging has another important effect. In general, it changes the ion potential of a given constituent in the alloy from its value in the pure state.[5] Such an effect must be included in any quantitative theory of alloys.

Jones[4] has given a perturbation calculation of the specific heat of alloys. We point out that perturbation theory is valid only when the charging or $\langle|V_{12}|\rangle/\Delta$ is small and not necessarily when the alloy is dilute. Jones's theory *cannot* be applied to alloys for which $\Delta Z/Z\gtrsim 1$, where ΔZ is the valence difference between the two constituents and Z is the smallest valence of the constituents, because then one expects the charging to be big in order to satisfy approximate charge neutrality. Thus Jones's theory should not be applicable to α-brasses and other noble-metal alloys that satisfy the Hume-Rothery rules. Experimental measurements on the residual resistance and the polar-reflection Faraday effect of Ag-Au alloys indicate that the properties in the vicinity of the Fermi surface of these alloys can be treated by perturbation theory, in agreement with the charging criterion. It has been shown that Jones's theory as applied to Ag-Au alloys does explain the

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specific-heat measurements. It would be useful to have measurements over a greater concentration range to verify more accurately the $\alpha(1-\alpha)$ dependence of the deviation from the linear interpolation.

Whereas the properties of the Ag-Au alloys in the vicinity of the Fermi surface can be calculated by perturbation theory, the experiments show that the properties of the *d*-bands cannot be treated by perturbation theory. The charging effect is large there. Each *d*-band state shows large charging effects, but because filled bands cannot have any net charging,[5] the actual change of the *d*-type states in the vicinity of each ion must be small. In the tight-binding approximation the total wave function of the solid with a completely filled band is always the same, independent of the amount of charging. In the more general case there could be some change in the wave function, depending on how large the charging is in individual states, but probably this is small. In Ag-Au alloys, since they can be treated in the tight-binding approximation, the total *d*-type wave function around each constituent should be closely the same as in the pure states, and these wave functions should accurately contribute the same to the potential "seen" by the *s*- and *p*-electrons as in the pure metals. Thus, the large charging in the individual *d*-band states does not change the fact that the electrons near the Fermi surface can be treated by perturbation theory.

If $V_{12}(\mathbf{k},\mathbf{l})$ is small compared with interband energies, and the angular frequency of light is much greater than the relaxation time of the electrons produced by $V_{12}(\mathbf{k},\mathbf{l})$, the optical properties of the alloy measured are those produced solely by the periodic part of the potential. The alloy "looks" optically like a pure metal with a periodic potential equal to the average potential in the alloy.

Specific-heat measurements, on the other hand, are affected by both the periodic and nonperiodic parts of the potential, and caution is needed in interpreting these measurements in terms of the density of states of the pure metals. Especially for the transition metals, measurement of the specific heat of alloys of two constituents with different valences has been used to infer information about the density of states of the pure metals assuming the rigid-band approximation. The applicability of this procedure to alloys that can be treated by the tight-binding approximation has been discussed elsewhere.[2,5] In this paper we have shown that even for alloys that can be treated by perturbation theory the alloy specific heat differs appreciably from that of the pure metal or of the "virtual pure metal" determined by the average potential. For alloys where perturbation theory does not apply—probably including all alloys of noble metals with atoms of larger valence—, we cannot expect any simple relationship between the specific heat of the alloy and the density of states of the pure noble metal. Certainly, a rigid-band model should not apply. There may be those who are disappointed by such a prospect. However, disordered alloys need not apologize for such a "shortcoming." After all, they, as examples of systems with no long-range order, are extremely interesting in their own right. By measuring their properties, it is not unreasonable to expect to determine simply the properties of alloys themselves!

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