PHYSICAL REVIEW VOLUME 157, NUMBER 3 15 MAY 1967

# Rigid-Band Model of Alloys

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(Received 23 December 1966)

The electronic structure of normal alloys is considered. This structure is divided into two categories, geometric and density of states. The geometric structure is the shape of constant-energy surfaces in reciprocal space. Under three conditions, the geometric structure of the alloys is the same as that of the pure solvent, but the density of states is different. These conditions are that: (a) the excess charge of the solute localizes around it; (b) the mean free path of the electrons is many interatomic spacings; (c) the electron states of interest in the pure solvent are in one band and are greatly separated in energy from the other bands. Under these same conditions, even when the electronic specific heat of dilute alloys is found experimentally to depend on only the electron per atom ratio and the change in volume produced by alloying as predicted by the rigid-band model, the value of the specific heat in the alloy still differs from the value given by the rigid-band model because the density of states of the alloy is different from that of the pure solvent. As a sideline of this investigation, it is pointed out that an expansion of the electronic structure of the alloy in terms of the concentration of the solute is not valid for concentrated alloys and only has validity in the dilute limit.

## I. INTRODUCTION

IN a pure metal, because of the periodicity of the lattice, the features of its electronic structure are well known. The single-particle states can be described in terms of Bloch states, the energy structure is characterized by Brillouin zone boundaries, energy gaps, energy bands, etc. In a disordered alloy, because of the destruction of the periodicity, none of these features are rigorously valid. However, it is known from both experimental and theoretical evidence[1] that these features of a perfectly periodic solid have approximate validity. At present, how approximate these ideas are has not been put on a completely quantitative basis and one has no good rule to decide how accurate it is to carry over ideas from pure metals to alloys and other disordered structures. The tendency has been to carry these ideas over without change till one runs into difficulty, and then to stop and scratch one's head. The most striking example of this is the use of the rigid-band model of alloys.[2] In the most elementary form of this model, it is assumed that the constant 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, thus swelling the Fermi surface and filling the density-of-states curve to a higher energy. As an example, in this model, the electronic structure for $\alpha$ brass consisting of say 10% zinc dissolved in copper, is obtained from that of pure copper with the first Brillouin zone filled to 1.1 electrons per atom instead of 1. The density of states of the alloy, proportional to its electronic specific heat, would be given by the density of states of pure copper at a Fermi energy corresponding to 1.1 electrons per atom. The shape of the Fermi surface of the alloy would be exactly the same as that of pure copper at a Fermi energy corresponding to 1.1 electrons per atom. Recent modifications of the rigid-band model[3] have suggested that the electronic structure is given instead by a periodic potential equal to the average of that of the two constituents weighted by their respective concentrations, all other features of the rigid-band model remaining the same.

In this paper the discussion of the rigid-band model is mainly directed toward the case of "normal" alloys where none of the constituents are transition metals. The applicability of the rigid-band model for transition metal alloys has been discussed in several papers[4] and there appears to be a qualitative understanding of when it is valid. However, such is not the case for the normal alloys. On one hand it seems to be fairly successful in explaining the Hume–Rothery rules,[2] and the changes in axial ratios in alloys of hexagonal crystal structure.[5] On the other hand, it is unsuccessful in explaining the value of the specific heats of normal alloys of the noble metals where the Hume–Rothery rules work.[6–10] In addition, the rigid-band model explanations of the Hume-Rothery rules[11] and the changes in axial ratios[12] have been questioned.

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[1] In reality even the purest obtainable materials are not perfectly periodic structures because of dislocations, point imperfections, impurities, etc. Yet, of course, their properties can be well described by the theory of perfectly periodic structures.

[2] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958), pp. 170–174; H. Jones, Proc. Roy. Soc. (London) **A147**, 400 (1934); Phil. Mag. **41**, 633 (1950).

[3] M. H. Cohen and V. Heine, Advan. Phys. **7**, 395 (1958).

[4] J. L. Beeby, Phys. Rev. **135**, A130 (1964); E. A. Stern, Physics **1**, 255 (1965).

[5] T. B. Massalski and H. W. King, Progr. Mat. Sci. **10**, 1 (1961).

[6] L. C. Clune and B. A. Green, Jr., Phys. Rev. **144**, 525 (1966).

[7] T. A. Will and B. A. Green, Jr., Phys. Rev. **150**, 519 (1966).

[8] B. A. Green, Jr., Phys. Rev. **144**, 528 (1966).

[9] B. W. Veal and J. A. Rayne, Phys. Rev. **130**, 2156 (1963).

[10] J. M. Ziman, Advan. Phys. **10**, 1 (1961).

[11] The explanation given in Ref. 2 assumes that the Fermi surface of the noble metals is free electronlike and the phase transformation occurs soon after contact of the Fermi surface with the zone boundaries. This argument, if unmodified, is no longer valid since we now know that in the pure noble metals, contact with the zone boundaries has already occurred.

[12] J. W. McClure, Phys. Rev. **98**, 449 (1955).

The specific heats of normal alloys of the noble metals have received much attention.[6–9] For the alloys such as the $\alpha$-phase alloys of silver with Cd and Sn, where the volume change versus electron per atom ratio[13] ($R$) is approximately the same, the initial percentage change in electronic specific heat is a function only of $R$, in spite of the greatly varying valency of the solutes. This agrees with the prediction of the rigid-band model. But the puzzling result which disagrees with the rigid-band model is that the electronic specific heat increases with $R$. It is generally agreed that because of the contact of the Fermi surface with the Brillouin zone boundaries in the noble metals, the density of states, and thus the electronic specific heat, should decrease with increasing $R$. Ziman[10] has made a detailed calculation for a simple model of the noble metals and shows that the peak in the density of states occurs at the energy whose surface in reciprocal space just touches the zone boundary. Below this energy the density of states increases with $R$, and above the energy, as per the situation for the noble metals, it decreases with $R$.

In this paper it is shown that under the right conditions—namely: (a) the excess charge of the solute localized around it; (b) the mean free path of the electrons is many interatomic spacings; (c) the electron states of the pure metal in the vicinity of the Fermi energy are in one band and are greatly separated in energy from other bands—all of the features of the rigid-band model are valid *except that the density of states in the alloy differs from that of the pure solvent.* The noble metals satisfy the above conditions and thus one can understand why the rigid-band model is so successful in explaining all of the properties of their normal alloys except their specific heats and other properties that depend on the density of states.

It is convenient to divide the predictions of the rigid-band model into two categories, geometric and density of states. The geometric predictions are those that use only the geometric properties of the constant energy surfaces such as the Hume-Rothery rules. The density-of-states predictions are related to those properties which depend on the density of states at the Fermi energy such as the electronic specific heat. The next section discusses the geometric aspects of the rigid-band model while Sec. III discusses the density of states of alloys when there is no volume change on alloying. The volume change on alloying case is discussed in Sec. IV. In Sec. V the experimental results on the normal alloys with the noble metals are discussed in light of the results of this paper. Section VI consists of a summary and discussion.

## GEOMETRIC STRUCTURE

In a pure metal the eigenstates are Bloch wave functions $\phi_k$ with energies $\epsilon_k$. When the periodicity of the pure metal is destroyed by alloying, these Bloch states are no longer eigenstates. This manifests itself by the energy of the Bloch states becoming complex,

$$\epsilon_k \rightarrow E_k + i\Gamma_k. \tag{1}$$

We can visualize the alloying process occurring by a number of atoms of the solvent picked at random having their potentials changed to that of the solute in a continuous fashion. Then the needed number of electrons can be added or subtracted to maintain charge neutrality. In this process the Bloch states $\phi_k$ change continuously to $\psi_k$ and $\epsilon_k \rightarrow E_k + i\Gamma_k$. The imaginary part $\Gamma_k$ shows that the Bloch state in the alloy $\psi_k$ is no longer an eigenstate but scatters into other states with a lifetime of the order of $(2\Gamma_k)^{-1}$. If the solute has a valency different from that of the solvent, perturbation theory is not valid[14] and the change from $\epsilon_k \rightarrow E_k + i\Gamma_k$ must be calculated by nonperturbative methods such as the Green's function method.[15] In any case, if $|\Gamma_k| \ll \Delta$, where $\Delta$ is the width of the band, then the Bloch states are approximately eigenstates and they can be used to calculate the properties of the alloys. For instance, the density of states of the alloy calculated by assuming $\Gamma_k = 0$ is in error of order $|\Gamma_k/\Delta|^2$ and thus is negligible if $|\Gamma_k| \ll \Delta$. For dilute alloys, $\Gamma_k$ is proportional to the fractional amount of solute $\alpha$, and the density of states is then in error of order of $\alpha^2$. Thus for very dilute alloys the error introduced by setting $\Gamma_k = 0$ is negligible. The criterion $|\Gamma_k/\Delta| \ll 1$ is equivalent to a long mean free path of the electrons at the Fermi energy of metals.

In what follows, we assume that $|\Gamma_k/\Delta| \ll 1$ and set $\Gamma_k = 0$. Consider the change in the energy of a Bloch state with alloying,

$$\Delta E_k = E_k - \epsilon_k. \tag{2}$$

Let us assume that $\Delta E_k$ depends only on $\epsilon_k$ and not on $k$:

$$\Delta E_k = \Delta E_k(\epsilon_k). \tag{3}$$

Then for the alloy a plot of $E_k$ versus $k$ will have the same shape of constant energy surfaces as for the plot of $\epsilon_k$ versus $k$ for the pure solvent. A given energy surface of the alloy will correspond to a different energy value from that of the same shaped surface of the pure solvent, but the shapes remain exactly the same. As the $R$ of the alloy is varied, the $k$ states in the alloy become filled up exactly in the same manner as those in the pure solvent. The Fermi surface would touch the zone boundaries at the same $R$ in both cases and the peak in the density of states would occur at the same $R$ in both cases. Since, in general, $\Delta E_k$ is not a constant, the *value* of the density of states in the two cases would not be the same, but its sharp structure, such as the maximum produced when the Fermi surface just touches the zone boundaries, would be the same.

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[13] In this paper $R$ is calculated by assuming that each constituent contributes to the conduction band all of its valence electrons.

[14] E. A. Stern, Phys. Rev. 144, 545 (1966).

[15] A. Seeger, *Metallic Solid Solutions*, edited by J. Friedel and A. Guinier (W. A. Benjamin Inc., 1963), paper VII.

Thus in such an alloy the rigid-band arguments of Jones[2] can be applied to explain the Hume–Rothery rules and the variation of the axial ratio in hexagonal alloys, both of which depend on only the geometric structure.

The question naturally arises under what conditions is the assumption in Eq. (3) valid. According to calculations using the Green's function method,[15] Eq. (3) appears to be valid when the perturbation is fairly localized about the solute site. Such is expected to be the usual case of the shielding by the conduction electrons of the solvent.

In the above discussion it has been implicitly assumed that the perturbation of the solute does not mix in states from other bands so that the number of states in the band below a constant-shaped energy surface remains the same. This will be the case if the states under consideration are well separated in energy from other bands. This is true even if bound states are formed below the band. As discussed by Friedel,[16] these bound states come from states at the bottom of the band and do not change the total number of states below a constant energy surface. Bound states cannot be approximated by $\psi_k$, i.e., $\Gamma_k$ cannot be neglected, and they cannot be represented as a point in reciprocal space. If the bound states come from states at the bottom of the band, a possible case when the valency of the solute is greater than that of the solute, they will be occupied and the alloy states in $k$ space are filled to the same energy surface since the number of states enclosed remains the same, bound state or not. If bound states are formed at the top of the band, a possibility if the valency of the solute is less than that of the solvent, they won't enter in as long as the Fermi energy is below their energy.

It is interesting to note that the alloy state $\psi_k$ does not have the same wave number $k$ as the corresponding state $\phi_k$ has, i.e., as the potential is varied from the pure solvent to that of the alloy the wave number of $\phi_k$ changes as it turns into $\psi_k$. This can be seen by remembering that the perturbations of the solute are localized. Thus there are regions where the potential is exactly the same as in the pure solvent, and in those regions the $E_k$ versus $k$ relations is the same as in the pure solvent. Since $E_k \neq \epsilon_k$, the wave number of $\psi_k$ in these regions is no longer $k$ but some different value $k'$ where $\epsilon_{k'} = E_k$. However, it is important to note that the plot of $E_k$ versus $k$ employed in the previous arguments is a plot of $E_k$ versus the $k$ that the corresponding state has in the pure solvent, and *not* versus $k'$.

## III. DENSITY OF STATES

If $\Delta E_k$ is a constant, the density of states of the alloy would have the same shape as that of the pure solvent but displaced in energy by $\Delta E_k$ and the rigid-band model would apply.[16] We will show that when the valency of the solute differs from that of the solvent, $\Delta E_k$ is not, in general, a constant and thus the density of states of the alloy will be different from that of the pure solvent, contrary to the rigid-band model. Before doing that we will present the expression of the density of states of the alloy in terms of $\Delta E_k$.

When the concentration of the solute $\alpha$ is small, $\Delta E_k$ is also small and we find for the density of states of the alloy $\rho(E)$

$$\rho(E) = \rho_0(E) - \left.\frac{\partial \rho_0(\epsilon_k)\Delta E_k(\epsilon_k)}{\partial \epsilon_k}\right|_{\epsilon_k = E}, \tag{4}$$

where $\rho_0(E)$ is the density of states of the pure solvent and the derivative is taken at constant $\alpha$. Our problem for determining $\rho(E)$ reduces to a determination of $\partial \Delta E_k(\epsilon_k)/\partial \epsilon_k$, since we assume that $\rho_0(E)$ is known.

We can determine a great deal about $\Delta E_k$ by use of very general arguments. First consider the case where addition of the solute does not change the lattice constant of the metal. Then the Fermi energy of a very dilute alloy is the same as that of the pure solvent even when the valence of the solute differs from that of the solvent.[16] This is because the perturbation of the solute is shielded within a short distance by a build-up of charge around it, and then outside of this distance the potential and density of electrons are the same as in the pure solvent. In fact, Friedel has shown that the Fermi energy change is proportional to $\exp(-K/\alpha^{\frac{1}{3}})$ for small $\alpha$ where $K$ is some constant.[16] Thus for small $\alpha$, the Fermi energy is constant. The exponential variation of the Fermi energy is related to the exponential shielding of the perturbations of the solute. The Fermi energy changes appreciably when there is appreciable overlap of the shielding electron clouds around neighboring impurities. This is expected only for concentrated alloys.

When a certain fractional concentration $\alpha$ of solute is added to a solvent of valency one, the $R$ is $1+\alpha Z$ where $Z$ is the excess valency of solute over that of the solvent. The first Brillouin zone, as per the arguments of Sec. II, becomes filled to the constant energy surface $\epsilon_k(\alpha Z)$ of the solvent where

$$N\alpha Z = \int_{E_F}^{\epsilon_k(\alpha Z)} \rho_0(E)dE \tag{5}$$

and $N$ is the number of atoms in the solid. However, in the alloy this constant energy surface is now the Fermi surface with energy $E_k = E_F + H(\alpha)$ where $H(\alpha)$ is the term proportional to $\exp(-K/\alpha^{\frac{1}{3}})$. Thus $\Delta E_k$ has the value from (2) of

$$\Delta E_k(\epsilon_k, \alpha Z) = E_F + H(\alpha) - \epsilon_k(\alpha Z), \tag{6}$$

where $\epsilon_k(\alpha Z)$ is given by (5), and $E_F$ is the Fermi energy of both the solvent and the alloy. In (6) we have written $\Delta E_k$ as a function of $\epsilon_k$ and $\alpha Z$, yet in general we expect that $\Delta E_k$ would be a function of the four

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[16] J. Friedel, Advan. Phys. 3, 446 (1954).

variables $\epsilon_k$, $\alpha$, $U(r)$, and $M$, where $U(r)$ is the perturbation introduced by the solute and $M$ is the mass of the solute. The mass could enter via the electron-phonon interaction. We show[16a] that in reality $\Delta E_k$ is a function of only the two variable $\epsilon_k$ and $\alpha Z$. For very dilute alloys $\Delta E_k$ can be expanded in a power series in $\alpha$,

$$\Delta E_k(\epsilon_k,\alpha,U,M)=\alpha F(\epsilon_k,U,M)+\alpha^2 G(\epsilon_k,U,M). \quad (7)$$

For the values of $\epsilon_k(\alpha Z)$ given by (5), $\Delta E_k$ has the value given by (6). When $\alpha$ is small enough, $H(\alpha)$ can be neglected and we obtain

$$E_F-\epsilon_k(\alpha Z)=\alpha F[\epsilon_k(\alpha Z),U,M] \\ +\alpha^2 G[\epsilon_k(\alpha Z),U,M] \quad (7')$$

The left-hand side of (7′) is only a function of $\alpha Z$ while the right-hand side appears to be a function of $\alpha$, $\alpha Z$, $U(r)$, and $M$. It is possible to vary both $M$ and $U(r)$ an infinite number of ways, keeping $Z$ and $\alpha$ fixed. The only way the equality in (7′) can hold is if $F$ and $G$ are not functions of such variations of $U(r)$ and $M$. Finally, since the left side of (7′) is only a function of $\alpha Z$, the right side also must be functions of only $\alpha Z$. Thus we can write (7′) as

$$E_F-\epsilon_k(\alpha Z)=\alpha Z f[\epsilon_k(\alpha Z)]+(\alpha Z)^2 g[\epsilon_k(\alpha Z)], \quad (8)$$

where $f(\epsilon_k)=F(\epsilon_k,U)/Z$, and $g(\epsilon_k)=G(\epsilon_k,U)/Z^2$. If we now permit $\epsilon_k$ and $\alpha Z$ to be independent variables by not requiring (5) to hold and using the relations in (8), Eq. (7) can be written

$$\Delta E_k(\epsilon_k,\alpha Z)=\alpha Z f(\epsilon_k)+(\alpha Z)^2 g(\epsilon_k), \quad (9)$$

where both $f$ and $g$ are only functions of $\epsilon_k$, and $\Delta E_k$ is only a function of $\epsilon_k$ and $\alpha Z$. In summary, using the result that in dilute alloys the Fermi energy remains fixed, we have shown[16a] that $\Delta E_k$ is only a function of $\epsilon_k$ and $\alpha Z$, instead of the possible four variables of $\epsilon_k$, $\alpha$, $U(r)$ and $M$. In other words, the effect of $U(r)$ enters only through $Z$ and in the combination $\alpha Z$ while the mass and thus all electron-phonon effects do not contribute at all.[16a] This is the case for constant volume. The effects of $U(r)$ and $M$ can enter indirectly by changing the volume as discussed in the next section.

By combining (9) with (4) we see that for dilute alloys

$$\rho(E_F)=\rho_0(E_F)-\alpha Z[\rho_0'(E_F)f(E_F) \\ +\rho_0(E_F)f'(E_F)], \quad (10)$$

where

$$\rho_0'(E)=\partial\rho_0(E)/\partial E; \quad f'(E)=\partial f(E)/\partial E$$

and the derivative is taken at constant $\alpha$. Since the coefficient of the linear term in temperature of the electronic specific heat $\gamma$ is proportional to $\rho(E_F)$, we can, from (10), write for dilute alloys,

$$\frac{d\ln\gamma}{dR}=-\frac{\rho_0'(E_F)}{\rho_0(E_F)}f(E_F)-f'(E_F), \quad (11)$$

a result independent of the type of solute in agreement with the rigid-band model, but with a value different from that given by the rigid-band model. Using (5) and expanding $\rho_0(E)$ to first order in $E-E_F$, we find that

$$N\alpha Z=\rho_0(E_F)(\epsilon_k(\alpha Z)-E_F) \\ +\tfrac{1}{2}\rho_0'(E_F)(\epsilon_k(\alpha Z)-E_F)^2. \quad (12)$$

We can combine (12) with (8) and solve for $f$ obtaining

$$f(E_F)=-[N/\rho_0(E_F)], \quad (13)$$

and (11) becomes

$$\frac{d\ln\gamma}{dR}=\frac{N\rho_0'(E_F)}{\rho_0^2(E_F)}-f'(E_F). \quad (14)$$

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[16a] *Note added in proof*: It was recently pointed out to the author by Hugh Montgomery and Ben Green, Jr., that the argument in Sec. III leading to the conclusion that the electron specific heat of dilute alloys is dependent on only $R$, the electron-per-atom ratio, is incorrect. This can be seen from Eq. (7′) by expanding $F(\epsilon_k,U,M)$ about $\epsilon_k=E_F$ to first order, obtaining

$$E_F=\epsilon_k(\alpha Z)=\alpha F(E_F,U,M)+\alpha F'(E_F,U,M)(\epsilon_k(\alpha Z)-E_F) \\ +\alpha^2 G(E_F,U,M), \quad (7'')$$

where

$$F'=\partial F/\partial\epsilon_k.$$

The left side of (7″) is correctly expanded to order $\alpha^2$. From Eq. (5) we find to first order in $\alpha$,

$$\epsilon_k(\alpha Z)-E_F=N_{\alpha}Z/\rho_0(E_F). \quad (5')$$

Substituting (5′) into (7″) we find to second order in $\alpha$,

$$E_F-\epsilon_k(\alpha Z)=\alpha Z f(E_F,U,M) \\ +(\alpha Z)^2\left[f'(E_F,U,M)\frac{N}{\rho_0(E_F)}+g(E_F,U,M)\right]$$

where $f=F/Z$ and $g=G/Z^2$ as in Eq. (8). The fact that the left side of Eq. (7″) is a function of only $\alpha Z$ assures that the coefficients of the $\alpha Z$ and $(\alpha Z)^2$ terms are independent of $U$ and $M$. This means that

$$f(E_F,U,M)=f(E_F)$$

and

$$f'(E_F,U,M)N/\rho_0(E_F)+g(E_F,U,M)=\beta(E_F), \quad (29)$$

where both $f(E_F)$ and $\beta(E_F)$ are independent of $U$ and $M$ in agreement with their explicit forms given in Eqs. (13) and (15). The second equation in (29) does not in general imply that $f'$ and $g$ are separately independent of $U$ and $M$ as incorrectly stated in the paper. The most general dependence implied by (29) is

$$f'(E_F,U,M)=\frac{\rho_0(E_F)\beta(E_F)}{2.5N}-\frac{\rho_0(E_F)}{N}g(E_F,U,M), \quad (30)$$

and thus $f'$ can also be a function of $U$ and $M$. This means from Eq. (11) that $d\ln\gamma/dR$ can also depend on $U$ and $M$. How important is the dependence on $U$ and $M$ cannot be determined from the reasoning used in this paper. A more detailed model-dependent calculation is required. However, the important result is still true that even if experimentally it is found that $d\ln\gamma/dR$ is dependent on only $R$, its value is still not expected to agree with the rigid-band model. In other words, a dependence of the electron specific heat on only $R$ is *not* evidence that the rigid-band model is valid. To summarize, the error made in the paper can be corrected by adding to every $f'(E_F)$ in the paper another term $h(E_F,U,M)$ which depends on the detailed shape of the potential and the mass of the impurity. $d\ln\gamma/dR$ can have some explicit dependence on the mass and the detailed shape of the potential of the impurity. All other statements in the paper remain unaffected.

The rigid-band model predicts only the first term in (14). For the noble metals,[10] $\rho_0'(E_F)<0$ and thus the rigid-band model predicts a negative value for $d\ln\gamma/dR$ in disagreement with experiments. The expression in (14) shows that there is an additional contribution which is proportional to $\partial\Delta E_k/\partial\epsilon_k$, the derivative being taken at constant $\alpha$, and physically represents the change in the shape of the density-of-state curve produced by alloying.

We can obtain a relation between $f'(E_F)$ and $g(E_F)$ by using (8) and (12), and expanding both $f$ and $g$ about $E_F$ in a power series of $(\epsilon_k(\alpha Z)-E_F)$, retaining terms to second order in $(\epsilon_k(\alpha Z)-E_F)$. In this manner we find that

$$f'(E_F)=\frac{N\rho_0'(E_F)}{2\rho_0^2(E_F)}-\frac{\rho_0(E_F)}{N}g(E_F) \tag{15}$$

and from (14)

$$\frac{d\ln\gamma}{dR}=\frac{N\rho_0'(E_F)}{2\rho_0^2(E_F)}+\frac{\rho_0(E_F)g(E_F)}{N}. \tag{16}$$

If the properties of $\rho_0$ for the solvent are known, then a measurement of $d\ln\gamma/dR$ can determine, using (15) and (16), $g(E_F)$ and $f'(E_F)$. This in turn determines the variation of $\Delta E_k(\epsilon_k,\alpha Z)$ in the vicinity of $E_F$ to first order in $\epsilon_k-E_F$ and to second order in $\alpha Z$. This can be seen by expanding $f(\epsilon_k)$ to first order in $\epsilon_k-E_F$ in (9) and using (13) to obtain

$$\Delta E_k(\epsilon_k,\alpha Z)=-\frac{\alpha ZN}{\rho_0(E_F)}+\alpha Zf'(E_F)(\epsilon_k-E_F)+(\alpha Z)^2g(E_F). \tag{9'}$$

The condition (6) which states that the Fermi energy remains fixed for dilute alloys is equivalent to Friedel's sum rule over phase shifts.[16] This condition of self-consistency, as we have shown,[16a] greatly restricts the possible dependence of $\Delta E$ on the type of solute. In fact it implies for fixed volume that $\Delta E$ depends only on the $Z$ of the solute and not on the details of its potential or the value of its mass. Thus the effective potential seen by such electrons, which consists of the potential of the solute plus the added potential of the screening electrons, produces the same Friedel sum of phase shifts for a given $Z$ and is not dependent on the detailed variation of the potential of the solute—a rather strong restriction. The screening of the potential clearly has an important contribution to the total effective potential and both quantitatively and qualitatively wrong results occur if this screening contribution is neglected.

In the above discussion the $H(\alpha)$ term in Eq. (6) has been neglected. This can be justified in the limit that $\alpha\rightarrow 0$ because then $H(\alpha)$ and all of its derivations go to zero, i.e., $H(\alpha)$ has an essential singularity at $\alpha=0$. From (6) we see that $\Delta E$ also has an essential singularity at $\alpha=0$. It, in addition, has an analytic part and in the vicinity of $\alpha=0$ the analytic part will dominate $H(\alpha)$. This can be verified by differentiating with respect to $\alpha$ both sides of (6) as many times as desired and setting $\alpha=0$. Such a procedure gives relationships between only the analytic parts of both sides of (6), the essential singularity contribution being always zero.

## IV. VOLUME CHANGES

When alloying changes the volume in addition to the $R$, the situation is more complicated. The perturbation effect of the solute is no longer localized. Its excess charge is localized by screening but the strain perturbation that it introduces locally has a long-range effect which contributes to the change in volume. As discussed by Eshelby,[17] about one third of the total volume change produced by a solute in a metal comes from a uniform change in volume of the solvent matrix and the rest of the volume change occurs in the immediate vicinity of the solute atom. In addition to the uniform volume change, the solvent matrix is distorted by a long-ranged shearing strain. With a random distribution of solute atoms, the shearing strain cancels out on the average and a cubic lattice remains cubic. However, microscopically, even far away from any solute atoms, the solvent matrix is distorted from a cubic lattice. This distortion and change in volume invalidates the arguments given previously in this section since the Fermi energy in the surrounding matrix will be different from that of the pure solvent and the Friedel sum rule is no longer valid. Call this new Fermi energy $E_F'$. For $\epsilon_k(\alpha Z)$ given by (5) one now has

$$\Delta E_k=E_F'-\epsilon_k(\alpha Z). \tag{17}$$

Imagine that one has a dilute alloy with a solute which produces a certain volume change per solute atom $C$. Further imagine that the $U(r)$ and $M$ of the solute are varied but maintaining the $Z$ and the volume change per atom $C$ the same. Then outside of the region where the excess $Z$ is shielded, the electron density and the electron potential are exactly the same as before because the strain remains exactly the same.[18] Thus using similar arguments as before[16a] the Fermi energy remains at $E_F'$ and (17) indicates the $\Delta E_k$ is still not an explicit function of $U(r)$ and $M$. One concludes[16a] that $\Delta E_k$ is a function of only $\epsilon_k$, $\alpha$, $Z$, and $C$. Volume changes can also be produced by changing the external pressure in addition to alloying. Volume changes by alloying affect the Fermi energy differently in two ways from that of pressure. Firstly, of the total volume change produced by alloying, only about one third of it is effective in changing the volume of the solvent matrix,

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[17] J. D. Eshelby, Phys. Rev. **25**, 255 (1954).
[18] H. Jones, Phys. Rev. **134**, A958 (1964).

while all of the volume change by pressure is transmitted to the matrix, and secondly, alloying introduces long-ranged shearing strains which are not present under pressure changes.

The above discussion can be summarized[16a] by saying that

$$\Delta E_k = \Delta E_k(\epsilon_k, \alpha, Z, C). \tag{18}$$

It is important to reiterate that the solvent matrix volume change is not the same as obtained from macroscopic measurements or from x-ray diffraction. The volume change in the solvent matrix $\Delta V'$ is given for an elastically isotropic solid by[17]

$$\Delta V'/\Delta V = \beta, \tag{19}$$

where $\beta = \frac{2}{3}(1-2\sigma)/(1-\sigma)$, $\Delta V$ is the total volume change, and $\sigma$ is Poisson's ratio.

If $C$ is very small, its effects on the solvent matrix can be treated by first-order perturbation which is equivalent to the virtual crystal model.[14] In the case considered here, the virtual crystal model, which employs a periodic potential equal to the average potential, is simply the pure solvent expanded by $\Delta V'$. The change in the density of states of the dilute alloy produced by the expansion $\Delta V$ to first order in $\alpha$ is then simply given by the change in properties of the pure solvent after an expansion $\Delta V'$. The total change in $\rho(E)$ with alloying becomes

$$\rho(E_F', V) - \rho_0(E_F, V_0) = \frac{\partial \rho_0}{\partial v_0}\Delta V' + \alpha Z\left[\frac{N\rho_0'(E_F)}{\rho_0(E_F)} - \rho_0(E_F) f'(E_F)\right], \tag{20}$$

where $V_0$ and $V$ are the initial and final volumes of the alloy, respectively, and the last term of (20) proportional to $\alpha Z$ is the same as in (10).

From the definition of $C$ we can write

$$\Delta V = \alpha C \tag{21}$$

and then from (19)

$$\Delta V' = \beta \alpha C. \tag{22}$$

We next calculate $d \ln\gamma/dR$ from (20) obtaining

$$\frac{d \ln\gamma}{dR} = \delta_0 \frac{\beta C}{V_0 Z} + K_0, \tag{23}$$

where

$$\delta_0 = \frac{\partial \ln\rho_0}{d \ln V_0} \quad \text{and} \quad K_0 = \left(\frac{N\rho_0'(E_F)}{\rho_0^2(E_F)} - f'(E_F)\right).$$

Using (21) we can write

$$\frac{C}{V_0 Z} = \frac{d \ln V}{dR} \tag{24}$$

and thus (23) becomes

$$\frac{d \ln\gamma}{dR} = \beta \delta_0 \frac{d \ln V}{dR} + K_0, \tag{25}$$

a linear relationship between $d \ln\gamma/dR$ and $d \ln V/dR$.

When $C$ is not small, its effects on the solvent matrix cannot be treated by first-order perturbation theory even when $\alpha$ is very small. Because of the long-ranged properties of the elastic strain, when the first-order effects of $C$ are of order $\alpha C$, the second-order effects are of order $\alpha C^2$. In this case the properties of the matrix are a function of $C$. This means that both $\delta_0$ and $K_0$ in (25) became functions of $C$ and one expects in general that

$$\frac{d \ln\gamma}{dR} = A(C)\frac{d \ln V}{dR} + B(C), \tag{26}$$

where $A(0) = \beta\delta_0$ and $B(0) = K_0$. From (24) we see that $C$ is dependent on both $Z$ and $d \ln V/dR$. Thus a plot of $d \ln\gamma/dR$ versus $d \ln V/dR$ will not give a single-valued curve for large $C$. Only for $C$ around zero will the plot be single-valued.

For comparison we give the rigid-band model expression for $d \ln\gamma/dR$. The rigid-band model would replace (20) by[8]

$$\Delta\rho_{\text{r.b.}} = \frac{\partial \rho_0}{\partial V_0}\Delta V + N\alpha Z \frac{\rho_0'(E_F)}{\rho_0(E_F)} \tag{27}$$

and then

$$\left.\frac{d \ln\gamma}{dR}\right|_{\text{r.b.}} = \delta_0 \frac{d \ln V}{dR} + \frac{N\rho_0'(E_F)}{\rho_0^2(E_F)}. \tag{28}$$

The rigid-band model predicts a single-valued and linear plot of $d \ln\gamma/dR$ versus $d \ln V/dR$.

## V. COMPARISON WITH EXPERIMENTS

The success of the geometric aspects of the rigid-band model in explaining changes in axial ratio in hexagonal alloys and the Hume–Rothery rules for phase changes is well known. Such a procedure is justified in Sec. II. Though the density of states differs from that of the pure solvent because $\Delta E_k$ is a function of $\epsilon_k$, the Fermi surface of the alloy touches the zone boundaries at the same $R$ as expected by the rigid-band model. This produces a peak in the density of states of the alloy at the same $R$ as the rigid-band model. The explanation of the Hume–Rothery rules requires only the maximum in the density of states and not that the density of states be the same as that of the pure solvent. The explanation of the change in axial ratio of hexagonal alloys requires overlap of electrons across Brillouin zone energy gaps. The use of such concepts for alloys has been justified in Sec. II. The successes of the geometric aspects of the rigid-band model are most notable for the noble metal-based alloys, in agreement with the three criterion stated in this paper. The noble

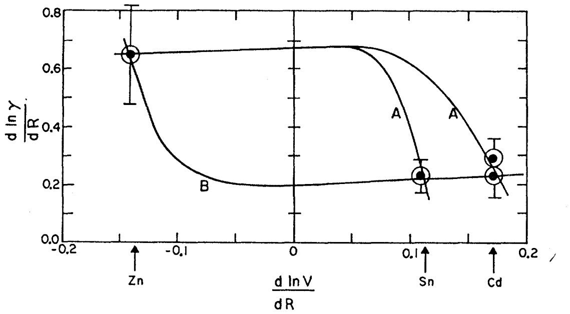

FIG. 1. The points are a plot of the experimental electronic specific-heat data of silver alloys. Curves $A$ and $B$ are two of many possible plots which satisfy the theoretically predicted slope at $d\ln V/dR=0$. Curve $A$ is double-valued consistent with the theory which predicts that $d\ln\gamma/dR$ depends on both $Z$ and $d\ln V/dR$. The values of $Z$ for Sn and Cd are 3 and 1, respectively.

metals best satisfy these conditions, in particular, the one requiring a large energy separation between the Fermi energy and states in other bands and the long-mean free path of the electrons.

The outstanding failing of the rigid-band model is in explaining the electronic specific heat of dilute alloys of the noble metals. The experiments[6–9] show that the electronic specific heat has an initial increase with an increase of $R$. The rigid-band model predicts, instead, a decrease because the Fermi surfaces of the noble metals are in contact with the Brillouin zone boundaries. Even a proposed modification of the rigid-band model,[3] wherein the shape of the constant energy surfaces changes with alloying, cannot explain the experiments.[10] Another striking feature of the experimental results shown in Fig. 1 is that if the rigid band is assumed to explain the variation of the specific heat with volume changes in alloying, then $\delta_0$ in (28) is approximately equal to $-1$. For a free-electron gas[8] $\delta_0=\frac{2}{3}$. As pointed out by Green,[8] the sign of $\delta_0$ is the same sign as expected for the electronic contribution to the thermal expansion. Copper has been measured to have a positive electronic thermal expansion and since the silver Fermi surface is more free electronlike than that of copper, one would also expect that Ag would have a positive value for $\delta_0$. Gold's Fermi surface is quite similar to that of copper and one would expect that Au also would have a positive value of $\delta_0$. The rigid-band model should then predict a *positive* slope when $d\ln\gamma/dR$ is plotted against $d\ln V/dR$ for the noble metals, yet the experiments indicate a negative slope.

TABLE I. Some noble metal alloys and their lattice dilatation and electronic specific-heat changes in the dilute limit. Errors shown in the specific-heat measurements are 95% confidence limits. Also shown for the pure noble metals are the values of Poisson's ratio $\sigma$, the quantity $\beta$ calculated by (19) and $\beta\delta_0$, which is the slope of $d\ln\gamma/dR$ versus $d\ln V/dR$ at $d\ln V/dR=0$, assuming that $\delta_0$ has the free-electron value of $\frac{2}{3}$.

| Metal | $\frac{d\ln V}{dR}$ | $\frac{d\ln\gamma}{dR}$ | $\sigma$ | $\beta$ | $\beta\delta_0$ |
|---|---|---|---|---|---|
| Ag | $\cdots$ | $\cdots$ | 0.37[h] | 0.28 | 0.19 |
| Ag-Cd | 0.17[g] | $0.29\pm0.07$[a] | | | |
| Ag-Cd | 0.17 | $0.22\pm0.08$[a] | | | |
| Ag-Sn | 0.11 | $0.22\pm0.06$[b] | | | |
| Ag-Mg | 0.081 | $\cdots$ | | | |
| Ag-Ge | 0.007 | $\cdots$ | | | |
| Ag-Ga | $-0.03$ | | | | |
| Ag-Zn | $-0.14$ | $0.65\pm0.17$[c] | | | |
| Au | $\cdots$ | $\cdots$ | 0.42 | 0.18 | 0.12 |
| Au-Sn | 0.10 | $0.82\pm0.14$[d] | | | |
| Au-Ge | 0.024 | $\cdots$ | | | |
| Au-Ga | $-0.02$ | $\cdots$ | | | |
| Au-Al | $-0.05$ | $\cdots$ | | | |
| Au-Zn | $-0.15$ | $\cdots$ | | | |
| Cu | $\cdots$ | $\cdots$ | 0.36 | 0.29 | 0.19 |
| Cu-Sn | 0.28 | $0.24\pm0.06$[e] | | | |
| Cu-Zn | 0.19 | $0.33\pm0.10$[f] | | | |
| Cu-Al | 0.10 | $\cdots$ | | | |
| Cu-Si | 0.02 | $\cdots$ | | | |
| Cu-Be | $-0.28$ | $\cdots$ | | | |

[a] From B. A. Green, Jr., and H. V. Culbert, Phys. Rev. **137**, A1168, (1965) using data of H. Montgomery and G. P. Pells, in Proceedings of the Conference on the Electronic Structure of Alloys, University of Sheffield, 1963 (unpublished).

[b] B. A. Green, Jr., and H. V. Culbert, Phys. Rev. **137**, A1168 (1965).

[c] Reference 8.

[d] Reference 7.

[e] Reference 6.

[f] Reference 9 as analyzed in Ref. 8.

[g] W. B. Pearson, *Handbook of Lattice Spacings and Structure of Metals and Alloys* (Pergamon Press, Inc., New York, 1958).

[h] *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), pp. 2–62 to 2–66.

These failings of the rigid-band model are explained by the theory proposed here. Alloying modifies the shape of the density-of-states curve and thus one expects a different variation of the electronic specific heat from that predicted by the rigid-band model. The increase of the electronic specific heat with alloying is a direct consequence of the presence of the $f'(E_F)$ term in (14). The experiments indicate that this term is negative producing a positive increase in $\gamma$ which overcomes the negative increase contributed by the first term on the right side of (14), which is the rigid-band term. The variation of $\gamma$ with $d\ln V/dR$ as plotted in Fig. 1 is more complicated. The rigid-band model predicts a linear variation but the theory presented here predicts a more complicated variation. Only for small values of $C=Z(d\ln V/dR)$ is a linear variation expected with slope $\beta\delta_0$. Using the free-electron value of $\delta_0=\frac{2}{3}$ and the value of $\beta$ listed in Table I we expect a positive slope near $d\ln V/dR=0$ of magnitude approximately 0.2. For larger values of $C$ we no longer expect a linear variation. It is clear from Fig. 1 that the experimental points do not uniquely determine the dependence of $d\ln\gamma/dR$. For instance one could plot many curves through the data which satisfy the theory presented here. Two such possible curves are plotted in Fig. 1 with the slope near $d\ln V/dR$ equal to 0.19 as predicted in this paper. Curve $A$ is double-valued as permitted theoretically while curve $B$ is single-valued which may also be the case if the curve is linear as shown. It is clear that the experiments are not definitive enough to verify the details of the theory presented here.

## VI. SUMMARY AND DISCUSSION

When a pure solvent is alloyed with a given solute, Bloch states are no longer rigorously valid eigenstates. However, if the mean free path of the electrons is many interatomic spacings, which will always occur for dilute alloys and may occur for more concentrated ones, Bloch states are good approximate eigenstates. The energy of these states will change with alloying and if this change is a constant independent of the state, the rigid-band model applies. There is no change in the constant energy surfaces in $k$ space and the shape of the density of states remains the same. Such may be the case if first-order perturbation theory applies.[16] However, if the solute has a different valency from the solvent, first-order perturbation theory is no longer sufficient and the rigid-band model cannot be entirely correct.[14] Second-order perturbation theory[14] has been applied to calculate the change in the density of states of alloys but such an analysis gives accurate results only when the constituents have the same valency.[14] This has been successfully applied to the Ag–Au alloy system.[14]

In the case where the valency of the solute differs from that of the solvent all of the features of the rigid-band model remain except that the shape of the density-of-states curve changes in the alloy. Under usual circumstances the change in the energy levels of Bloch states, $\Delta E_k$, is a function only of the original energy and not its position in $k$ space. Thus, constant energy surfaces of the pure solvent remain so in the alloy when plotted in the $k$ space of the pure solvent. Of course, the energy value corresponding to a given surface changes with alloying. If the lifetime of the Bloch states is long, the density of states of the alloy is given to good approximation by the same integral over $k$ space as for the pure solvent and characteristic structure in both it and the pure solvent occur at the same $R$. An example of such structure is the maximum in the density of states when the Fermi surface just touches the zone boundary.

The shape of the density-of-states curve in the alloy changes with alloying because the spacing between energy levels changes. It is shown,[16a] however, that for a given solvent, the density of states near the Fermi energy and thus the electronic specific heat of dilute alloys is a function of only $R$, the volume change per atom, and $\alpha$ the fractional atomic concentration of the solute. This is shown by use of an argument which is a generalization of the one that leads to the Friedel sum rule. Such an argument includes all many-body effects such as electron-electron and electron-phonon interaction. These many-body effects and differences in the solute potentials for a given $Z$ can manifest themselves only by causing a strain in the solvent matrix.[16a] In order to produce different effects they must produce different strains. The only possible way for this argument to break down is if $\Delta E_k$ is not simply a function of $\epsilon_k$ but also depends on $k$, i.e., the constant energy surfaces change shape with alloying. Such a situation appears highly unlikely based on model calculations.[15]

In studying the electronic structure of alloys, it is common to expand in powers of the concentration and to assume that such an expansion converges. From the fact that with no matrix strain the Fermi energy changes with concentration, as $e^{-\kappa/\alpha^{\frac{1}{3}}}$, and the relationship of this with $\Delta E_k$ as discussed in Sec. III, one concludes that $\Delta E_k$ also has a term of the form $e^{-\kappa/\alpha^{\frac{1}{3}}}$. Such a term cannot be described by a power series expansion about $\alpha=0$, and when it becomes important, such a power series is no longer valid. This occurs when there is appreciable overlap between the screening clouds of electrons around the impurities, i.e., for concentrated alloys. We therefore conclude that expanding the electronic structure in powers of the concentration has validity only for dilute alloys and breaks down for concentrated alloys.

The analysis of the experiments in Sec. V makes it abundantly clear that there are insufficient experiments to prove or disprove the theory presented here. The most definitive test would be to determine the slope of a plot of $d\ln\gamma/dR$ versus $d\ln V/dR$ at $d\ln V/dR=0$. Theoretical estimates of this slope for the noble metals are listed in Table I. This could be done for Ag alloys by measuring the specific heats of Ag–Ge, and Ag–Ga as listed in Table I. The theory presented here predicts this slope to be 0.19 for Ag.

It has been proposed that the $\gamma$ of alloys may depend explicitly on the ratio of the solvent to solute masses.[7] The theory presented here[16a] says that $d\ln\gamma/dR$ is a function of only $d\ln V/dR$ and $Z$. It would be possible to determine the correct parameters by measurement on a sufficient number of alloys.

Although the discussion in this paper has been limited to binary alloys, a straightforward extension of the same reasoning to ternary alloys indicates that $\gamma$ would be a function of the variables $(R-1)$, $\alpha$, $C_1$ and $C_2$, where $C_1$ and $C_2$ are the volume changes produced per atom of each of the two solutes, respectively. In this case it is possible to keep the volume constant but vary the other variables. For example, assuming, as one expects for dilute alloys, that the volume of ternary alloys can be found by linear extrapolation between the binary alloys, adding Zn and Cd atoms to silver in the proportion of 17 to 14, respectively, should produce an alloy with no volume change. Also, adding Zn and Sn atoms to silver in the proportion of 11 to 14/3, respectively, should also produce an alloy with no volume change. Yet, in both cases it is predicted by the theory presented here that $d\ln\gamma/dR$ will differ from the value found in Ag–Ge alloys which also have no volume change.