PHYSICAL REVIEW VOLUME 188, NUMBER 3 15 DECEMBER 1969

Electronic Properties of Alloys*

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(Received 20 January 1969; revised manuscript received 29 August 1969)

The well-known criterion for characterizing approximately the electronic properties of concentrated alloys in pure-metal terms is that the mean free path of the electrons be many atomic spacings. For alloys whose solvent and solute have different valences, this condition can be expressed in terms of the energy shift $\Delta E(\mathbf{k})$ of a given Bloch state as the impurities are adiabatically turned on. The criterion in terms of $\Delta E(\mathbf{k})$ is that its real part should be much greater than its imaginary part, which is satisfied if that part of the t matrix of the solutes which contributes to real scattering is small. The noble-metal alloys that obey the Hume-Rothery rules satisfy this weak-scattering criterion because the shielding cloud around dilute heterovalent impurities is more spread out than expected on the free-electron model, enhancing higher-angular-momentum phase shifts. Such a spreading of the shielding cloud is a consequence of band effects introduced by a large energy gap between the conduction band and the next unoccupied band. The small t matrix or phase shifts cannot be calculated by perturbation theory because the change of wave function in the vicinity of the impurity is large; yet once they are known, their effects can be treated as small. It is shown for this type of alloy that a Bloch state with wave vector $\mathbf{k}$ in the pure metal will have exactly the same $\mathbf{k}$ in the alloy as the solutes are adiabatically turned on. The response of this alloy to electric and magnetic fields can be calculated from the same formulas as are used for pure metals, with the substitution of a phenomenological relaxation time appropriate for the alloy, and with energy levels of the alloy $E(\mathbf{k})=E_0(\mathbf{k})+\Delta E_r(\mathbf{k})$ in place of the energy levels of the pure metal $E_0(\mathbf{k})$, where $\Delta E_r(\mathbf{k})$ is the real part of the energy shift $\Delta E(\mathbf{k})$. In particular, de Haas-van Alphen measurements determine the shape of the Fermi surface of the alloy, which in general differs from that of the rigid-band model.

I. INTRODUCTION

INTEREST in the study of alloys has increased greatly in the last few years. The reason for this is not too hard to ascertain. Our fundamental understanding of disordered alloys and other disordered systems is quite primitive compared to that of the pure solids. As the investigations in pure solids become more detailed and more quantitative, the contrast with disordered systems becomes more glaring. In the study of disordered alloys, the noble-metal-based alloys have a prominent position. Many of their experimental properties can be explained by the simple rigid-band model.[1] In fact, the famous Hume-Rothery rules are mainly applicable to the noble-metal alloys.[1] The Hume-Rothery rules state that the various boundaries of the stability of phases in the noble-metal alloys occur at approximately the same electron-per-atom ratio $\mathfrak{z}$ independent of the alloying element. More examples of Hume-Rothery-type rules have been found in the changes of the axial ratios with $\mathfrak{z}$ in some hexagonal noble-metal alloy phases.[2] All of these properties have a simple explanation in terms of the rigid-band model. Briefly, if we can treat the disordered alloy as a pure material we can describe the states of the alloy in terms of Bloch states. In the simple rigid-band model the alloy is assumed to have the same electronic structure as the pure host with a Fermi surface determined by the $\mathfrak{z}$ of the alloy. The alloy phase boundaries correspond to the value of $\mathfrak{z}$ where some part of the Fermi surface is in the vicinity of touching the Brillouin-zone boundaries. The change in the axial ratio corresponds to the value of $\mathfrak{z}$ where electron states above an appropriate gap energy just start to be occupied.

It has been shown that in order to explain the experimental data, it is not necessary to assume as extreme a model as the rigid-band model.[3] In fact, only the geometric part of the rigid-band model need be assumed. The geometric part refers to the shape of constant-energy surfaces in k space and if these are approximately the same in the alloy as in the pure host, the explanation of the experimental data still follows. In a previous publication,[3] it was pointed out that the geometric structure of alloys is the same as the host if three conditions are fulfilled. These are (a) the excess charge of the solute localizes around it; (b) the mean free path of the electrons is many atomic spacings; and (c) the electron states of interest in the pure solvent are in one band and are greatly separated in energy from the other bands. In this paper it will be pointed out that in the sense that condition (a) was used, it and condition (b) are inconsistent for noble-metal alloys. Condition (a) assumed that the excess charge of the heterovalent solute was so localized that essentially only s-wave-type scattering occurred and thus the shift of the energy was such that constant-energy surfaces in the pure host remained so in the alloy. What we show here is that when such strong localization of charge occurs, condition (b) will not be satisfied for concentrated alloys. In order to maintain condition (b), condition (a) must be modified to

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* Research sponsored in part by the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, under AFOSR Grant No. AF-AFOSR-1270-67.

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permit an increased spread in the excess charge around the impurity so that higher-order orbital-angular-momentum waves can scatter with an appreciable amplitude. This spread in shielding charge is greater than that predicted for a free-electron-gas model of the noble metals, yet, as discussed in Sec. II, the effect of the noble-metal band structure is to produce such a spread of the shielding charge around impurities. This modification of condition (a) is expected to produce a change in the shape of the constant-energy surfaces on alloying. Yet such a change in the geometric structure on alloying does not invalidate the Hume-Rothery rules. After all, the original explanation of the Hume-Rothery rules[1,4] incorrectly required that the Fermi surface of the pure noble metals not touch the zone boundaries, yet the predictions of this theory still agreed reasonably well with experiments. The explanation of the Hume-Rothery rules apparently does not depend too critically on the shapes of the constant-energy surfaces as long as they are reasonably close to those of the pure host. However, this point requires more experimental and theoretical investigation.

The outline of the paper is as follows: Section II discusses how the modification to the shielding cloud around the impurity introduced by the band structure of the noble metals decreases the scattering. Section III presents a theory of the properties of alloys in the weak-scattering limit. In Sec. IV a comparison between theory and experiment is made. The summary and conclusion is presented in Sec. V.

II. BAND-STRUCTURE EFFECTS

In calculating the properties of solids, much success has been attained by assuming that every interaction is shielded in a manner characteristic of a free-electron gas.[5] The fact that the electrons in a solid are not free but are moving in a periodic potential does not appreciably affect the shielding in many cases. However, in the case of the noble-metal alloys, the periodic potential and the resultant band structure have an important effect as we discuss here.

The critical characteristic of the noble metals which distinguishes them in this case is the large energy separation between the conduction band and the higher unfilled bands. We idealize the discussion by assuming that the conduction band is so far separated from all other bands that these other bands can be entirely neglected. The model that we discuss is a metal with a single band whose properties can be calculated in the tight-binding approximation (TBA). Such an approximation is not accurate for the *s*-*p* electrons of the noble metals, but the results of this model can still be applied by replacing the TBA atomic states with the appropriate Wannier functions of the alloy. We consider an alloy composed of two constituents which are distributed on a simple Bravais lattice in a random fashion. We thus neglect interstitial alloys, volume distortion, or short- and long-range order effects. We will illustrate our point by considering the dilute impurity limit, but our qualitative result will remain true for all compositions and for all types of alloys. The discussion in this section depends heavily on Ref. 6.

In the TBA the wave function for the pure metal can be written as

$$\psi_k(\mathbf{r})=\sum_a e^{i\mathbf{k}\cdot\mathbf{R}_a}\phi_1(\mathbf{r}-\mathbf{R}_a)\,, \tag{1}$$

where $\phi_1(\mathbf{r}-\mathbf{R}_a)$ is the atomic wave function of the type-1 constituent of which the pure metal is composed. The atoms are centered at the points of the lattice $\mathbf{R}_a$. We assume for simplicity that ϕ_1 is an s function. The band corresponding to the ψ_k can hold two electrons per atom when the two spin states of the electrons are included. We assume that the type-1 atom contributes only one electron per atom to this band.

Now, let us replace one of the type-1 atoms centered at $\mathbf{R}_s$ by a different atom of type 2 which contributes two electrons per atom. We assume that the atomic wave function of the type-2 atom is $\phi_2(\mathbf{r}-\mathbf{R}_s)$. The general wave functions of the alloy $\Omega_m(\mathbf{r})$ can be written in the TBA as

$$\Omega_m(\mathbf{r})=\sum_n a_n(m)\phi_n(\mathbf{r}-\mathbf{R}_n)\,, \tag{2}$$

where $\phi_n=\phi_1$ for all $n\neq s$ and $\phi_n=\phi_2$ for $n=s$. Here $a_n(m)$ are constants independent of $\mathbf{r}$. Corresponding to each Ω_m there is the eigenenergy E_m. At 0°K the $N+1$ states in the band of lowest energy will be occupied where N is the number of lattice sites. The one excess electron contributed by the impurity at R_s will be localized in its vicinity due to the Coulomb attraction with the positive charge of the impurity atom. What is of interest is how this one excess electron charge is distributed among the Ω_m. In the free-electron gas, the states near the Fermi energy pile more charge in the vicinity of the impurity than far away from it to build up the total shielding charge.[7] In particular, if an additional electron is added to the electron gas, its state would also have a larger amplitude in the vicinity of the impurity as it penetrates the shielding charge and feels the attractive potential.

What we now show is that if an additional electron is added to the metal in our model, its state would have a *smaller* amplitude in the vicinity of the impurity than away from it. This follows almost immediately from the theorem[6] that in a completely filled band there are exactly two electrons around every atom for

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both the impurity and the host atoms. This theorem simply states that one cannot put more than two electrons in the atomic states ϕ. If all the shielding charge is localized around the impurity in the state ϕ_2, then it is completely occupied and the addition of any further electrons to the system would require them to have states which deposit no charge on the impurity site. This is too extreme a situation, as more detailed calculations show.[6] Not all of the shielding charge is localized in the state ϕ_2 and additional electron states have a nonzero amplitude on the impurity. However, the amplitude on the impurity will be less than on the other atoms. By continuity, one also expects that states at the Fermi energy have this same type of amplitude behavior.

The t matrix which determines the scattering from the impurity is given by[8]

$$t_{k'k}=\langle\phi_{k'}|V(r)|\psi_k\rangle\,, \tag{3}$$

where $\phi_{k'}$ is an unperturbed Bloch state and ψ_k is the actual initial state as modified by the screened impurity perturbation $V(r)$. From the above discussion we expect

$$|t_{k'k}|^2<|\langle\phi_{k'}|V(r)|\phi_k\rangle|^2 \tag{4}$$

at the Fermi energy because ψ_k is decreased compared to ϕ_k in the region where $V(r)$ is large. In Sec. III we discuss the properties of alloys with small t-matrix elements as in relation (4).

The experimental evidence gives strong confirmation that band-structure effects on shielding are important in the noble metals as discussed in Sec. IV.

III. WEAK SCATTERING-LIMIT IN ALLOYS

If we consider a state $|\mathbf{k}\rangle$ in the pure host with energy $E_\mathbf{k}$, as the impurities are adiabatically turned on, the energy of this state changes to $E(\mathbf{k})=E_\mathbf{k}+\Delta E(\mathbf{k})$. The weak-scattering limit is defined by the condition that

$$\mathrm{Re}\Delta E(\mathbf{k})\equiv\Delta E_r(\mathbf{k})\gg \mathrm{Im}\Delta E(\mathbf{k})\equiv\Delta E_i(\mathbf{k})\,. \tag{5}$$

The magnitude of $\Delta E_i(\mathbf{k})$ is a measure of the scattering of the state $|\mathbf{k}\rangle$ in the alloy. Small values of $\Delta E_i(\mathbf{k})$ signify a long lifetime or small scattering. In terms of the t matrix of Eq. (3), the condition (5) means that

$$\mathrm{Re}t_{kk}\gg \mathrm{Im}t_{kk}\,. \tag{6}$$

This is shown in the Appendix by proving that in the dilute limit $\Delta E(\mathbf{k})=N_it_{\mathbf{kk}}$, where N_i are the members of impurities.

Let us introduce the Green's function for the alloy:

$$G=(E-H)^{-1}\,, \tag{7}$$

where H is the Hamiltonian of the alloy. Then from the definition of $E(\mathbf{k})$,

$$\langle\mathbf{k}|G|\mathbf{k}\rangle=1/[E-E(\mathbf{k})]\,. \tag{8}$$

Let us define H_A by

$$H_A=H_0+\sum_\mathbf{k}|\mathbf{k}\rangle\Delta E(\mathbf{k})\langle\mathbf{k}| \tag{9}$$

and G_A by

$$G_A=(E-H_A)^{-1}\,, \tag{10}$$

where H_0 is the Hamiltonian of the pure host.

G_A has the same diagonal elements as G. They are related to one another by

$$G=G_A+G_A(H-H_A)G\,. \tag{11}$$

Introducing the T matrix by[9]

$$TG_A=(H-H_A)G\,, \tag{12}$$

we have

$$G=G_A+G_ATG_A\,. \tag{13}$$

By calculating the diagonal elements of both sides of (13), we determine that

$$\langle\mathbf{k}|T|\mathbf{k}\rangle=0\,. \tag{14}$$

Now let us define a new Hamiltonian H_A' which is the real part of H_A:

$$H_A'=H_0+\sum_\mathbf{k}|\mathbf{k}\rangle\Delta E_r(\mathbf{k})\langle\mathbf{k}|\,. \tag{15}$$

Letting

$$G_A'=1(E-H_A')\,, \tag{16}$$

we can write (13) as

$$G=G_A'+G_A'TG_A'+O(\Delta E_i)\,, \tag{17}$$

where the remainder is of the order of ΔE_i. Equation (17) implies that

$$\psi_\mathbf{k}=|\mathbf{k}\rangle+G_A'T|\mathbf{k}\rangle+O(\Delta E_i)\,, \tag{18}$$

where $\psi_\mathbf{k}$ is an eigenstate of the alloy. Taking the dot product of $\langle\mathbf{k}|$ with both sides of Eq. (18) we obtain

$$\langle\mathbf{k}|\psi_\mathbf{k}\rangle=1+O(\Delta E_i)\,. \tag{19}$$

Equation (19) informs us that in the weak-scattering limit, $\psi_\mathbf{k}$ has approximately the same $\mathbf{k}$ as that of the state $|\mathbf{k}\rangle$. Now the energy of $\psi_\mathbf{k}$ is E, while that of $|\mathbf{k}\rangle$ is $E=E_\mathbf{k}+\Delta E_r(\mathbf{k})$ in the alloy and $E_\mathbf{k}$ in the pure host. In other words, $|\mathbf{k}\rangle$ is the adiabatically related state to $\psi_\mathbf{k}$. Thus we have proved that, in the weak-scattering approximation, the $\mathbf{k}$ for a state in the pure host remains the same in the alloy as the impurities are turned on.

We can define a T' such that (18) can be written in the form

$$\psi_\mathbf{k}=|\mathbf{k}\rangle+G_A'T'|\mathbf{k}\rangle\,. \tag{20}$$

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Table I. Phase shifts. Comparison between calculated and experimental phase shifts for impurities in noble metals with a valence difference of Z. The calculated values assume free-electron shielding in the Thomas-Fermi model and are obtained from Ref. 16. The experimental values are obtained by matching theory with experimental data in Ref. 15. The data in the table is the data in Ref. 15 corrected to the case of no volume change in alloying by multiplying all phase shifts of a given impurity by the same factor. The experimental values are for: $Z=1$, Cd in Ag; $Z=2$, In in Ag; $Z=3$, Sn in Ag; and $Z=4$, Sb in Ag.

	$Z=1$		$Z=2$	
	Free-electron calculation	Expt.	Free-electron calculation	Expt.
δ_0	1.055	0.247	2.139	0.393
δ_1	0.143	0.294	0.290	0.603
δ_2	0.029	0.064	0.053	0.130
δ_3	0.007	0.014	0.012	0.031
δ_4	0.002	0.003	0.003	0.008
	$Z=3$		$Z=4$	
	Free-electron calculation	Expt.	Free-electron calculation	Expt.
δ_0	2.826	0.477	3.401	0.571
δ_1	0.459	0.936	0.673	1.267
δ_2	0.074	0.201	0.093	0.271
δ_3	0.017	0.047	0.021	0.063
δ_4	0.004	0.011	0.005	0.015

In the weak-scattering limit, T' will be small. Formally, (20) is equivalent to $|\mathbf{k}\rangle$ with energy $E_r(\mathbf{k})$ being scattered by a weak potential equal to T', and it is known that the Boltzmann equation can be applied to such a case.[10] This is discussed in more detail in the Appendix. The Boltzmann equation can be used to calculate the transport properties of the alloy in the weak-scattering limit. Moore[11] shows a similar result up to fourth order in the potential. Our discussion here is applicable to all orders in the potential.

In addition, all of the other results of pure solids with weak scattering can be used. This includes the definition of a Fermi surface, the interpretation of the de Haas-Van Alphen effect in terms of the extremal cross section in k space, the optical mass at frequencies below interband ones,[12] and the polar-reflection Faraday effect[13] in terms of an appropriate integral over the Fermi surface. What must be remembered, however, is that the geometric structure, i.e., the constant-energy surfaces in k space or the $E(\mathbf{k})$ relations, *must be those of the alloy.*

IV. COMPARISON WITH EXPERIMENT

Noble-metal alloys are unique because of the large energy gap between the conduction band and the next unoccupied band. According to the discussion of Sec. II, this causes the states at the Fermi energy to deposit less than average charge near the center of a heterovalent impurity. Any shielding must occur further away from the impurity which enhances the higher partial-wave scatterings. The Friedel sum rule[14]

$$Z=2/\pi \sum_l (2l+1)\delta_l(k_F)\,, \tag{21}$$

where Z is the valence difference between the impurity and the host, and $\delta_l(k_F)$ is the phase shift at the Fermi momentum, indicates that by spreading the phase shifts to the higher l values, it is possible to keep all phase shifts small and still satisfy the sum rule. This would not be the case if only δ_0 were important. We expect most phase shifts to be positive for an attractive potential as would be the case for a multivalent impurity in a noble-metal matrix. A phase-shift analysis of experimental data[15] as shown in Table I, shows that small phase shifts are a good approximation for a $Z=1$ impurity (an impurity with valence two). For $Z=2$ impurities the approximation is still quite good, while for $Z=3$ impurity the approximation of small phase shifts is marginal. The importance of band-structure effects in keeping all phase shifts small, as discussed in Sec. II, becomes evident by comparing with phase shifts calculated for a free-electron gas,[16] as in Table I.

Calculations of the orbital susceptibility of dilute noble-metal alloys using a free-electron model[16] give poor agreement with experiment. The authors presumed that this poor agreement was caused by the neglected band characteristics of the Cu electrons. The discussion in this paper agrees with this presumption. The band characteristic of the Cu electrons does improve the theory of orbital susceptibility by introducing a greater spreading of the shielding cloud which increases the diamagnetic contribution, as required by experiment.

Other independent evidence of the band-structure modification of the shielding cloud in the vicinity of the impurity is given by electrical-resistance measurements. Impurities in the noble metals produce a residual resistivity change of about $\frac{1}{4}$ the value calculated from the Born approximation.[17] The same calculation for host metals of Mg, Al, and Pb give a more reasonable agreement.[17] These latter metals have small band gaps and overlapping bands so that one expects that the free-electron theory would be reasonable, as is the case. The smaller measured residual resistivity of the noble metals can be explained by a spreading out of the shielding cloud and a repulsion of the wave function at the impurity as expected from band-structure effects. Such a modification of the wave functions would increase the higher-angular-momentum partial-wave scattering at the expense of the $l=0$ partial

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wave. These higher-angular-momentum partial waves contribute less to the resistance because of the $1-\cos\theta$ factor that enters in the theoretical calculation.

The determination of electron scattering on different parts of the Fermi surface by de Haas–van Alphen measurements also confirms the band-structure effects on electron shielding. The electron states on the belly have mainly s symmetry about the Cu cores, while those on the neck have mainly p symmetry.[18] The shielding of $Z=0$ impurities such as Ag in Cu would not be greatly affected by the band-structure effects. Only $Z\geq 1$ impurities saturate the band allowance of two electrons around each atom and thus their shielding is greatly affected by the band. We expect then that $Z=0$ impurities would have more localized shielding clouds than $Z\geq 1$ impurities. This distinction can be proved by observing the belly and neck electrons. The s-type belly electrons will be more strongly scattered by a localized shielding charge than the p-type neck electrons and vice versa. Thus one expects that for $Z=0$ impurities, the ratio of the belly electron scattering to neck electrons will be greater than for $Z\geq 1$ impurities. The experimental data agree with this. The ratio of the scattering temperature (which is proportional to scattering) of the neck X_N to that of the belly X_B is found to be[19]

$$X_N/X_B \approx 1.5 \tag{22}$$

for polyvalent impurities, while

$$X_N/X_B \approx \tfrac{1}{2} \tag{23}$$

for homovalent impurities which do not change the volume.[20]

In the weak-scattering approximation, a state of wave vector $\mathbf{k}$ in the pure solvent ends with the same wave vector $\mathbf{k}$ after the impurities are adiabatically turned on, i.e., as the number of solvent atoms are adiabatically converted to impurity atoms in a continuous fashion. In addition, the uncertainty in $\mathbf{k}$ introduced by the alloying is much smaller than the shift in Fermi wave number produced by alloying. However, in general, one expects that the constant-energy surfaces in the alloy change shape from those of the pure solvent because the energy shift is not the same for all states of a given energy, i.e., $\Delta E_r(k)$ varies with k for a fixed E_k. We thus do not expect that, in general, the rigid-band model will predict accurately the shape of constant-energy surfaces in alloys. Interestingly, the de Haas–van Alphen experimental results of dilute alloys in Cu[19] agree with the rigid-band model to about 10%. One expects some deviation from rigid-band behavior and it would be interesting to make further de Haas–van Alphen measurements with Ag and Au as the hosts to see if nonrigid-band behavior can be observed.

The Hume-Rothery rules have a very natural explanation in terms of the band-structure effects present in the noble metals. All explanation of these rules assume that the alloy electronic band structure can be described in the same terms as used for pure metals. This means that a wave vector and its corresponding energy $E(\mathbf{k})$ can be defined. Such a definition must be valid, not only in the dilute limit but also in the concentrated regime where the $\mathfrak{z}$ has increased by about a factor of 2. This can occur only if the Bloch-like states have long mean free paths of many atomic spacings even in the concentrated regions. In terms of the energy shift in alloying, this requires that the real part be much greater than the imaginary part, which, in turn, is the definition of the weak-scattering limit. As the discussion in this paper indicates, such behavior follows for valence-1 metals when the conduction band is well isolated from the nearest occupied band. Since only the noble metals among the common metals have this property, we can understand why the Hume-Rothery rules best apply to the noble metals.

It is important to distinguish the noble metals from polyvalent metals, some of whose alloys also appear to satisfy rules which mainly depend on $\mathfrak{z}$. Long mean free paths of electrons in concentrated alloys of the polyvalent metals may also occur. In this case the long mean free paths occur because the impurity can be treated by perturbation theory. Perturbation theory is valid when the wave-function change in the vicinity of the impurity is small.[21] In the noble metals with polyvalent impurities, one expects a large change in wave function because there is percentagewise a large change in the charge density in its vicinity. However, for the case of, say, aluminum impurities (valence 3), in lead (valence 4), the percentage change of charge density is expected to be about 25%, which implies a change in wave-function amplitude of about 12.5%. Such a change one could expect to treat by perturbation theory, implying that a virtual-crystal or average-potential approximation would be valid. The scattering is thus small because the perturbation is small.

Another way to consider the case of polyvalent alloys is in terms of scattering phase shifts.[22] For aluminum impurities in lead, the shielding should be free-electron-like because the gaps in lead are small. For aluminum which has three electrons around it, the two s states are mostly filled.[22] The electrons at the Fermi surface in the vicinity of the Al impurity have only a small amount of s character, more p character and some d character. Thus one expects that the $l=1$ and larger phase shifts are appreciable, permitting small phase shifts to satisfy the Friedel sum rule (21). In this case, in contrast to the noble-metal alloys, the

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shielding is free-electron-like and the small phase shifts can be estimated by perturbation theory.

The criterion that we expect the Hume-Rothery noble-metal alloys to satisfy is that the change in k_F induced by alloying be much larger than the uncertainty of k. This point is discussed further in a later paper where a detailed comparison with experimental data will be made.

There are some positron annihilation data on Cu-Al alloys[23] and polar-reflection Faraday-effect measurements on Ag-Mg alloys,[24] both of which preliminarily indicate increased Fermi-surface neck size with increased $\mathfrak{z}$. Such behavior is predicted by this paper.

V. SUMMARY AND CONCLUSIONS

The behavior of the noble-metal alloys in satisfying the Hume-Rothery rules can be attributed to their unique property of a large energy gap between the conduction band and the nearest unoccupied band. This fact introduces band-structure modifications on the shielding of polyvalent impurities which has two related effects. The shielding charge is spread out further and the electrons at the Fermi energy have a smaller amplitude around the center of the impurity than expected on the basis of a free-electron model. These cause a weaker scattering of the electrons by the impurities. The scattering is weak enough that the t matrix can be treated by perturbation theory. It is important to emphasize that the t matrix itself is quite different from the V matrix, i.e., the actual perturbing potential. This is because the modifications of the wave functions near the impurities are large and cannot be treated by perturbation theory. From the weak t matrix and thus weak scattering, it follows that it is justified to describe the alloy in terms of k states, Fermi surface, Brillouin-zone boundaries, energy gaps, etc. Such arguments are necessary to justify the explanations[1,3,4] of the Hume-Rothery-type properties of the noble-metal alloys which depend only on $\mathfrak{z}$.

It should be emphasized that the band-structure effect on shielding occurs only for impurities with $Z \geq 1$. In these cases the shielding cloud saturates the band allowance of two electrons per atom. For impurities with $Z=0$, such as noble metal in noble metal, the band effects should not be important and the shielding should be similar to free-electron behavior.

The arguments used here are valid only for nontransitional impurities. It is assumed that in adiabatically turning on the impurities, various k states in the pure metal have approximately the same relative values of energy as in the alloy. In particular, the d states which are well below E_F remain so in the alloy. This will not be true for transition-metal impurities. For these impurities some of the d states in the noble-metal alloys can be shifted above E_F. To estimate the changes in electronic properties in this case one must calculate how the d states are shifted, a much more difficult program.

Although the small t-matrix alloys maintain to a good approximation the same $\mathbf{k}$-vector states as in the pure metal, the shape of the constant-energy surfaces is expected to change somewhat. However, this change should not appreciably modify the Hume-Rothery arguments.[1,3,4]

Because of the small t matrix, the interpretation of experiments is the same as is standard for pure materials with the following modifications. The added constituent acts as a scattering mechanism which can be treated phenomenologically by the standard device of a relaxation time. The alloy has a Fermi surface whose size and shape is such as required to enclose the $\mathfrak{z}$ of the alloy using the k space of the pure solvent but using the $E(k)$ of the alloy.

Throughout this paper the effects of volume changes have been neglected.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge a stimulating discussion with Professor Morrell H. Cohen.

APPENDIX

In this Appendix we give a more detailed proof that, when the t matrix of the impurities is small, the response of the alloy to electric and magnetic fields can be calculated by exactly the same formulas as derived for Bloch states if the value of the energy used is that of its adiabatically related alloy state.

A wave packet of $\psi_{\mathbf{k}}$ in Eq. (20) can be formed and from standard results[25] it will have a group velocity given by

$$\mathbf{v}(\mathbf{k}) = (1/\hbar)\nabla_{\mathbf{k}} E_r(\mathbf{k}), \qquad \text{(A1)}$$

where, it is important to note, $E_r(\mathbf{k})$ is the real part of the energy of the state in the *alloy*. This group velocity $\mathbf{v}$ is the velocity of an alloy electron in the state $\mathbf{k}$. We note that, although $\mathbf{k}$ does not change on alloying, the velocity does because the energy does.

The equation of motion of the alloy state $\psi_{\mathbf{k}}$ will be determined by the standard method of power conservation.[26] Electric fields $\boldsymbol{\varepsilon}$ and magnetic induction fields $\mathbf{B}$ exert a force $\mathbf{F}$ on the electron,

$$\mathbf{F} = e\boldsymbol{\varepsilon} + e\mathbf{v}(\mathbf{k}) \times \mathbf{B}, \qquad \text{(A2)}$$

where e is the electric charge of the electron. The power input into the alloy system by these fields acting upon an electron in state ψ_k is

$$P = \mathbf{F} \cdot \mathbf{v}(\mathbf{k}) = [e\boldsymbol{\varepsilon} + e\mathbf{v}(\mathbf{k}) \times \mathbf{B}] \cdot \mathbf{v}(\mathbf{k}). \qquad \text{(A3)}$$

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[23] D. L. Williams, E. H. Becker, and P. Petijevich, Bull. Am. Phys. Soc. **14**, 402 (1969).

[24] J. Tracy and E. Stern (unpublished).

[25] W. R. Smythe, *Static and Dynamic Electricity* (McGraw-Hill Book Co., New York, 1950), pp. 463–4.

[26] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Co., New York, 1940), p. 318.

The rate of change of energy of the alloy system caused by these forces on ψ_k is

$$P=dE_r(\mathbf{k})/dt=\nabla_k E_r(\mathbf{k})\cdot(d\mathbf{k}/dt)=\mathbf{v}(\mathbf{k})\cdot[e\boldsymbol{\varepsilon}+e\mathbf{v}(\mathbf{k})\times\mathbf{B}]. \tag{A4}$$

Using (A1) we see that one solution of (A4) is

$$\hbar(d\mathbf{k}/dt)=[e\boldsymbol{\varepsilon}+e\mathbf{v}(\mathbf{k})\times\mathbf{B}]. \tag{A5}$$

The term with **B** does not rigorously follow from (A4) since its dot product with **v** gives zero. We do, however, have the result that **B** does not change the energy of the state ψ_k, i.e., **B** causes **k** to remain on a constant-energy surface of the *alloy*.

That the contribution of **B** to (A5) is correct can be shown from a calculation of power absorption in a system moving with a constant velocity $\mathbf{v}(\mathbf{k})$. In such a system the velocity of the electron is now $\mathbf{v}'(\mathbf{k})=0$ and the electric field $\boldsymbol{\varepsilon}'=\boldsymbol{\varepsilon}+\mathbf{v}(\mathbf{k})\times\mathbf{B}$. We find from power conservation that the value of $\hbar(d\mathbf{k}/dt)$ produced by $\boldsymbol{\varepsilon}'$ is as given by (A5). But in the moving system, $d\mathbf{k}/dt$ is the same as in the stationary one, proving the validity of (A5). This argument could be criticized since in the moving system the electron is at rest and the power absorption is zero. To overcome this criticism the moving system can be chosen to have some infinitesimal velocity relative to the electron in a direction other than that of $\mathbf{v}(\mathbf{k})$.

If we consider constant **B** fields and $\boldsymbol{\varepsilon}$ fields which vary in time as the real part of $e^{-i\omega t}$, where $\hbar\omega$ is less than interband energies, we can write a Boltzmann equation for the alloy electron which treats scattering effects in terms of a phenomenological relaxation time τ,

$$\frac{\partial f}{\partial t}+\nabla_{\mathbf{r}}f\cdot\mathbf{v}+\nabla_{\mathbf{k}}f\cdot(e\boldsymbol{\varepsilon}+e\mathbf{v}(\mathbf{k})\times\mathbf{B})\hbar^{-1}=\frac{(f_0-f)}{\tau}, \tag{A6}$$

where $f(\mathbf{k},\mathbf{r})$ gives the occupation probability that the state **k** is occupied at the point **r** and f is the equilibrium distribution. We note that for $\omega\tau\gg1$, (A6) is the same Boltzmann equation as for the pure metal, except that alloy energies, and thus velocities, are employed. Thus all formulas which are derived from the Boltzmann equation for the pure metal in the limit of $\omega\tau\gg1$ are also valid for the alloy when the alloy energies and velocities are substituted for those of the pure metal.

Using (A5) and the fact that **k** in the alloy is the same as that in the pure metal, the states in a **B** field can be quantized following the same semiclassical derivations as for the pure solid.[27] One finds that the period of the de Haas–van Alphen effect is that calculated for the pure metal with the constant-energy surfaces of the alloy substituted for those of the pure metal. Thus the de Haas–van Alphen effect measures the maximum or minimum cross section of the constant-energy surfaces of the alloy. These are not the same as those given by the rigid-band model unless the constant-energy surfaces of the pure metal retain their same shape in the alloy. As discussed in Sec. IV this is not expected to be generally the case for alloys.

Equation (A5) coupled with the fact that **k** in an alloy is the same as in the pure metal indicates that ω_c, the cyclotron frequency, will change with alloying because $\mathbf{v}(\mathbf{k})$ changes. A calculation of the de Haas–van Alphen effect for an alloy as described in Ref. 28 neglects to take this into account and is therefore in error.

We now derive a form of the Friedel sum rule for dilute impurities with a small t matrix. Electron states at the Fermi energy in the pure metal have their energies shifted below E_F in the alloy when the impurities add Z more valence electrons per impurity atom than that contributed by the host atoms. This is true because when the impurity does not change the volume, as we have been assuming throughout, the Fermi level remains fixed. But we know that the Fermi surface for the alloy plotted in the same k space as the pure metal must contain more electrons to accommodate the n_1Z added by the impurities per unit volume, where n_1 is the number of impurities per unit volume. The original Fermi surface enclosed less electrons, and thus, on the average, the energies of these states in the alloy must be less than E_F. A state which in the pure metal has an energy $E_F-\Delta E_r(\mathbf{k})$ will be at the Fermi surface in the alloy. We require that the number of new states enclosed by the alloy Fermi surface just accommodate the electrons added by the impurities,

$$n_1Z=-\frac{2}{\hbar(2\pi)^3}\int_{E_F}\frac{dS\,\Delta E_r(\mathbf{k})}{\mathbf{v}_0(\mathbf{k})}, \tag{A7}$$

where $\mathbf{v}_0(\mathbf{k})$ is the velocity in the pure metal and dS is an element of area in k space on the Fermi surface of the pure metal. For a free-electron gas, (A7) reduces to the usual form of the Friedel sum rule in terms of phase shifts.

A general expression for $\Delta E(\mathbf{k})$ is[29]

$$\Delta E(\mathbf{k})=\langle\mathbf{k}|V|\psi_{\mathbf{k}}\rangle/\langle\mathbf{k}|\psi_{\mathbf{k}}\rangle, \tag{A8}$$

where $V=\sum_n V_n$ is the potential introduced by the impurities. In the dilute limit we can expand all quantities in (A8) as a power series in N_1, the number of impurities. Doing this and keeping just the lowest terms, we have

$$\langle\mathbf{k}|V|\psi_{\mathbf{k}}\rangle=\sum_n\langle\mathbf{k}|V_n|\psi_{\mathbf{k}}\rangle\approx N_1t_{\mathbf{kk}}, \tag{A9}$$

$$\langle k|\psi_k\rangle=1+O(N_1/N).$$

Substituting (A9) into (A8), we find

$$\Delta E(\mathbf{k})=N_1t_{\mathbf{kk}}. \tag{A10}$$

Substituting (A10) into (A7), our form for the Friedel

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[27] L. Onsager, Phil. Mag. 43, 1006 (1952).

[28] A. D. Brailsford, Phys. Rev. **149**, 446 (1966).

[29] Reference 7, p. 7.

sum rule becomes

$$Z=-\frac{2}{\hbar(2\pi)^3}\int_{E_F}\frac{dS\,\mathrm{Re}t_{\mathbf{kk}}}{v_0(\mathbf{k})}. \qquad \text{(A11)}$$

We note from (A7) that the average value of $\mathrm{Re}t_{\mathbf{kk}}$ depends on only Z, the valence charge difference between the impurity and the host, and not on the details of the potential. When $Z=0$, $t_{\mathbf{kk}}$ can be small and one expects that it can be calculated from perturbation theory. However, for $Z\neq 0$ in the noble metals, $t_{\mathbf{kk}}$ cannot be small and, as we argued in Sec. II, cannot be calculated from perturbation theory. Nevertheless, the total scattering by the t matrix could still be small, i.e., $t_{\mathbf{kk}'}$, could be small for most $\mathbf{k}'$ as discussed in Sec. II. The Friedel sum rule fixes the average value of $t_{\mathbf{kk}}$ at an appreciable value for $Z\neq 0$ and $t_{\mathbf{kk}'}$ then must go rapidly to small values as $\mathbf{k}'$ moves away from $\mathbf{k}$. Thus t produces scattering which is strongly peaked in the forward direction.

PHYSICAL REVIEW VOLUME 188, NUMBER 3 15 DECEMBER 1969

Alternative Transition-Metal Pseudopotential*

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(Received 16 June 1969)

We consider the pseudopotential interaction between the s-like electrons in metals that also contain d electrons, using Hubbard's hybrid representation of the Korringa-Kohn-Rostoker (KKR) band-structure method, in a manner similar to that recently employed by the author in discussing the total energy of d-band metals. The interaction is formulated as a sum of two parts: (1) a direct interaction between orthogonalized plane waves (OPW's), which is similar to the "transition-metal pseudopotential" recently defined by Harrison from a modified OPW viewpoint, and (2) an indirect interaction via the d electrons, similar to Harrison's "hybridizing terms." We then combine these two parts and arrive at the KKR-Ziman form of the pseudopotential as the resultant effective interaction. The author's previous result for the total energy of an alkaline earth or noble metal is reinterpreted as the consequence of using the KKR-Ziman pseudopotential with a d-scattering resonance.

I. INTRODUCTION

THIS paper is concerned with calculating the effective pseudopotential interaction between the s-like electrons in transition and near-transition metals, where the presence of the d bands in the electronic structure must be taken into account. Harrison[1] has treated this problem by considering the band structure from a modified orthogonalized-plane-wave (OPW) point of view, where the basis set of functions contains both OPW'S and atomiclike d functions[2]; he has in this way derived an effective pseudopotential interaction between the OPW states. Here we begin instead with the band structure represented by Hubbard and Dalton's[3,4] hybrid secular equation, which is based on a transformation of the Korringa-Kohn-Rostoker (KKR) method, and we formulate the pseudopotential interaction in these terms; the procedure employed is a generalization of that used by the author in deriving an expression for the total energy of the alkaline earth and noble metals.[5]

We obtain the pseudopotential interaction as the sum of two parts: The first part represents a direct interaction between OPW's and is similar to Harrison's[1] transition-metal pseudopotential; the second part represents an indirect interaction via the d electrons, similar to the hybridizing terms of Harrison's treatment. These two parts are then combined, and it is shown that the resultant effective pseudopotential reduces to the KKR-Ziman[6] (KKRZ) pseudopotential containing the full phase shift, including the d-scattering resonance, which is the result to be expected. Our previous expression for the total energy of an alkaline earth or noble metal can then be reinterpreted as the consequence of using the KKRZ form of the pseudopotential with a d-scattering resonance.

II. EFFECTIVE INTERACTION BETWEEN OPW'S

In the KKR method of band-structure calculation the muffin-tin approximation is used; the one-electron crystalline potential is approximated by a sum of non-

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* Supported in part by the U. S. Army Research Office (Durham), under Contract No. DA-HCO4-69-C-0007.

[1] W. A. Harrison, Phys. Rev. **181**, 1036 (1969).

[2] See, e.g., R. A. Deegan and W. D. Twose, Phys. Rev. **164**, 993 (1967).

[3] J. Hubbard, Proc. Phys. Soc. (London) **92**, 921 (1967).

[4] J. Hubbard and N. W. Dalton, J. Phys. **C1**, 1637 (1968).

[5] R. A. Deegan Phys. Rev. **186**, 619 (1969).

[6] J. M. Ziman, Proc. Phys. Soc. (London) **86**, 337 (1965).