

which agrees with Eq. (28) in PB-II, except for a factor $(-1/m)$ that is due to a trivial difference in our definition of \mathbf{F} .

IV. DISCUSSION

Equations (17), (19), or (20) are exceptionally valuable since they provide an immediate qualitative interpretation for some of the recent experimental results on the infrared and Raman spectra of mixed crystals.

For example, in the case of Raman scattering from a crystal with a single Raman-active mode the intensity of the scattered radiation $I(\omega)$ is proportional to $\text{Im}(\mathbf{G}(c, \omega^2 - i\epsilon, \mathbf{k}=0))_{\sigma_R, \sigma_R}$.²¹ From the single-impurity problem one knows local modes, or resonance modes, appear when $\mathbf{f}(0)$ has a singularity. From Eq. (17) it follows that $\mathbf{G}(c)$ must also have a singularity near the frequency for the resonant, or local, mode. It follows that the intensity $I(\omega)$ has peaks near these singularities. Thus the observation of new Raman lines in mixed Si:Ge crystals¹⁰ can be interpreted by either the local-mode theory or the random crystal theory. On the other hand, for some defects $\mathbf{F}(c)$ remains small for all fre-

quencies and to first order in the concentration

$$I(\omega) \sim \text{Im}[\omega^2 - i\epsilon - \omega_R^2 + c\mathbf{F}'(c=0, \omega^2 - i\epsilon)_{\sigma_R\sigma_R}]^{-1}, \quad (31)$$

where (for these type of defects) $\mathbf{f}(c=0) \approx \sum_i \mathbf{v}_i$. The Raman spectrum of mixed CaF_2 : SrF_2 crystals, in which no new lines appear,⁹ can be interpreted by (18). Similar considerations also apply to the case of infrared absorption by the lattice if σ_R is replaced by the index for the infrared-active branches.

The condition that $(1 + \mathbf{G}_0 \mathbf{v}_i)^{-1} \approx 1$ [see Eq. (17)] implies that $\mathbf{F}(c) \approx c \sum \mathbf{v}_i$. This constitutes a condition under which the "virtual-crystal approximation" will be valid for a given mixed crystal. From Eq. (20) one can see that this approximation could be valid for some phonons and not for others. Possibly one can explain the results^{9,25} in CaF_2 - SrF_2 and the results²⁶ on ZnS - ZnSe by just such considerations.

ACKNOWLEDGMENT

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²⁵ H. W. Verleur and A. S. Barker, *Phys. Rev.* (to be published).

²⁶ O. Brafman, I. F. Chang, G. Lengyel, S. S. Mitra, and E. Carnall, Jr., *Phys. Rev. Letters* **19**, 1120 (1967).

Electron States in Dilute Disordered Alloys*

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A simple model is considered of an alloy consisting of a free-electron gas with a dilute concentration of impurities. Electron states at the Fermi energy have a spread in wave numbers which blurs the Fermi surface. Only up to second order in perturbation theory is the average wave number of an alloy state the same as that given by the rigid-band model. A renormalization of the alloy wave function occurs which decreases the weight of that part of the state that is associated with a given wave number. The effect of renormalization shows itself in positron-annihilation experiments in alloys as an apparent decrease in the number of electrons in the vicinity of the Fermi momentum.

I. INTRODUCTION

IN discussing the properties of disordered alloys it is common to use the concepts and terminology of pure metals. Thus it is common¹⁻⁴ to refer to the Fermi surface, Brillouin zone, etc., of disordered alloys. The most striking example is that of the use of the rigid-band

model where the alloy is assumed to have the same electronic band structure as that of the pure host metal. Any additional electrons added by alloying are assumed to cause the Fermi surface calculated from the pure host to swell to accommodate the additional electrons. In a recent paper⁴ the range of validity of the rigid-band model is discussed. It is shown that under appropriate conditions the geometric aspects of the rigid-band model are expected to be valid. The geometric aspects are those that use the geometric properties of the constant energy surfaces in k space. In that paper it was emphasized that the k space used in the rigid-band model has no simple relationship to any wave number of the actual alloy wave function. In this paper we investigate what this relationship is. In order to get

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¹ N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958), pp. 170-174.

² 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 E. A. Stern, *Phys. Rev.* **157**, 544 (1967).

some insight into this question it is useful to start from a pure metal and to follow changes as the alloying proceeds. We do so in this paper for a simple model of a free-electron gas with a dilute number of impurities. We do not limit ourselves to the Born approximation but permit the potential of the impurities to be strong.

In Sec. II, the properties of the alloy wave function are discussed. In Sec. III, the interpretation of positron-annihilation experiments in alloys is presented. Section IV consists of a summary.

II. ALLOY WAVE FUNCTION

In discussing the Fermi surfaces of alloys we must be able to define some wave vector in whose space we can plot the constant energy surface with a value equal to the Fermi energy. For periodic structures this wave vector \mathbf{k} is the one associated with the Bloch state $\phi_{\mathbf{k}}$ defined by

$$\phi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}_n) = e^{i\mathbf{k}\cdot\mathbf{R}_n}\phi_{\mathbf{k}}(\mathbf{r}). \quad (1)$$

Here \mathbf{R}_n is a lattice vector such that the lattice at the points $\mathbf{r}+\mathbf{R}_n$ looks exactly the same as at the point \mathbf{r} . For alloys we will see that at least three different wave vectors naturally arise as contestants for the variables in terms of which the energy is represented. To aid in understanding the properties of alloys we choose the simplest possible nontrivial model. The interaction between electrons is neglected except as they enter into shielding the ionic potentials. The pure material is a free-electron gas and the alloy is produced by inserting a dilute concentration of impurity atoms into the electron gas at random positions. We assume that the potentials of the impurity atoms have spherical symmetry.

It is useful to imagine that the alloy is formed in the following sequence. The impurities with their electrons are added to the pure metal matrix, but the interaction between them is assumed initially to be turned off. Thus the electrons added by the impurities spread throughout the alloy and become additional free electrons causing the Fermi sphere to swell to a larger diameter to accommodate them. We call this the rigid-band model. Then the interaction between the impurities and the electrons is turned on in a continuous and gradual fashion until it reaches its final value. At this point the impurities will have localized electron-shielding clouds in their vicinities and the alloy is in its final and correct configuration.

In the rigid-band model the Fermi wave number in the alloy k_F has been increased over that of the original electron gas by the increase of the electron density. Because we are assuming that the impurities are present in only a dilute concentration the change in electron density is small and we can then approximate the increase in the Fermi wave number by

$$[2/(2\pi)^3]4\pi k_0^2 \Delta k_F = n\alpha Z, \quad (2)$$

where k_0 is the Fermi wave number of the pure metal, $\Delta k_F = k_F - k_0$ is the increase of the Fermi wave numbers in the rigid-band model of the alloy, n is the number of electrons per unit volume in the pure metal, $n\alpha$ is the number of impurities per unit volume, and Z is the positive charge of the ion core of the impurity atom in units of the negative of the electron charge. In an actual substitutional alloy, Z is to be interpreted as the difference in valence between the host and the impurity. Our assumption of a dilute concentration of impurities means that each impurity with its screening cloud of electrons is far separated from all of the others. The screening cloud and the self-consistent potential of each impurity are the same as for a single impurity in the metal. Since our impurities are inserted in a random fashion there will be in reality some impurities close enough together so that their interaction is not negligible. However, the number of such cases will be proportional to α^2 , and we assume that α is small enough that α^2 can be neglected compared to it. Thus our assumption of a dilute alloy permits us to characterize the impurity potential by the same machinery of the isolated impurity problem, i.e., a set of phase shifts as defined in scattering theory. In terms of these phase shifts the Friedel sum rule⁵ is

$$Z = -\frac{2}{\pi} \sum_l (2l+1) \delta_l(k_F), \quad (3)$$

where $\delta_l(k_F)$ is the phase shift of the l th partial wave at the Fermi surface. For the rigid-band model of the alloy each electron state

$$\phi_{\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}} \quad (4)$$

can be characterized by a wave vector \mathbf{k} , where $\hbar\mathbf{k}$ is the momentum of the state. The actual alloy of course does not have such eigenstates, but we can make a one-to-one correspondence between the states of the alloy and those of the rigid-band model in two different ways. For one, consider a state \mathbf{k} in the rigid-band model which has the energy

$$E_0(\mathbf{k}) = \hbar^2 k^2 / 2m. \quad (5)$$

In a continuous fashion let the rigid-band model transform to the actual alloy. In this process the state $\Phi_{\mathbf{k}}$ transforms to another state $\chi_{\mathbf{k}}$, and the energy $E_0(\mathbf{k})$ goes to $E(\mathbf{k}) + i(\frac{1}{2}\Gamma(\mathbf{k}))$. The energy becomes complex because a current-carrying state such as $\chi_{\mathbf{k}}$ cannot be an eigenstate in the alloy. The imaginary part $\Gamma(\mathbf{k})$ is a measure of the lifetime of the state due to scattering. In our dilute approximation $\Gamma(\mathbf{k})$ will be linear in α . This way, which establishes a correspondence between the rigid-band model and the alloy, we will call the adiabatic way.

The second way to make a correspondence we will call the dielectric way and it is as follows: Imagine the alloy in the form of a slab of finite thickness surrounded

⁵ J. Friedel, *Advan. Phys.* **3**, 446 (1954).

on both sides by the pure metal. In the region of the pure metal the electron can be described in terms of the Φ_k state of Eq. (4). An electron in state Φ_q impinging on the alloy will scatter as it enters the alloy. The combination of the scattered and incident waves will give the actual wave function of the system. Inside the alloy slab one expects in general that the coherent part of the wave will be attenuated and also be changed in wavelength, in analogy with the optical problem of light passing through a dielectric slab. From scattering theory⁶ the actual wave function ψ_q is

$$\psi_q(\mathbf{r}) = \phi_q(\mathbf{r}) + \int G_0(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \psi_q(\mathbf{r}') d^3r', \quad (6)$$

where G_0 is the Green's function or propagator in the pure metal and

$$V(\mathbf{r}) = \sum_i V_0(\mathbf{r} - \mathbf{r}_i) \quad (7)$$

is the potential of the impurities. We assume dilute impurities so that we can neglect overlap of shielding clouds and thus can assume that V is a sum of the potentials of isolated impurities V_0 centered at \mathbf{r}_i .

The assumption of dilute impurities permits an approximation in evaluating (6). The state ψ_q can be divided into two parts, a coherent and an incoherent part. The coherent part consists of the incident wave Φ_k plus the forward part of the scattered wave contributed by the last term in (6). The sum of the incident and forward scattered wave gives a coherent wave with a new wave vector K given by⁷

$$K^2 = q^2 + 4\pi n\alpha f_0, \quad (8)$$

where f_0 is the forward-scattering amplitude of the impurity potential V_0 and is given in terms of the phase shifts δ_l by

$$f_0 = -\frac{1}{k} \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l} \sin \delta_l. \quad (9)$$

In treating the incoherent part of the wave we take advantage of the diluteness of the alloy and use the dilute scattering approximation to calculate quantities to first order in α . In this approximation the wave function incident on a given impurity atom is $e^{i\mathbf{k}\cdot\mathbf{r}}$, the incident part of the wave function only. The incoherently scattered waves from other impurity sites produce a negligible contribution at the impurity site of interest because of their diluteness. This incident wave is scattered from each impurity site as though the impurity were isolated, giving as our total wave function

$$\psi_q(\mathbf{r}) = A e^{i\mathbf{K}\cdot\mathbf{r}} + \sum_i \int G_i'(\mathbf{r}, \mathbf{r}') V_0(\mathbf{r}' - \mathbf{r}_i) e^{i\mathbf{q}\cdot\mathbf{r}'} d^3r'. \quad (10)$$

Here A is a renormalization constant, and $G_i'(\mathbf{r}, \mathbf{r}')$ is

⁶ M. L. Goldberger and K. M. Watson, *Collision Theory* (John Wiley & Sons, Inc., New York, 1964), p. 75.

⁷ M. Lax, *Rev. Mod. Phys.* **23**, 287 (1951).

the electron propagator of energy $E_0(q) = \hbar^2 q^2 / 2m$ for a single impurity in the pure metal centered at \mathbf{r}_i with the forward-scattering part subtracted out. The forward-scattering part of G_i has already been incorporated into the coherent part $e^{i\mathbf{K}\cdot\mathbf{r}}$. Thus a knowledge of the single-impurity scattering problem is sufficient to approximate the wave function in dilute alloys.

One should note that the dilute approximation is distinct from the Born approximation. In both cases the incident wave function scattered at the impurity is assumed to be the unperturbed part only. However, in the Born approximation the scattering from an impurity is treated by perturbation theory while in the dilute approximation this scattering is treated exactly—in terms of phase shifts—as, say, in our case.

It is informative to look at the alloy in still another way, similar to the one used in deriving the Friedel sum rule. The perturbing potentials due to the impurities are localized about each impurity, and, in the dilute case, there is a region surrounding each impurity where the potential seen by an electron is that of the pure metal. In this region the solution of the Schrödinger equation for energy $E_0(q) = \hbar^2 q^2 / 2m$ is a state with wave number q . Yet from (10) we see that the wave number in the alloy for energy $E(q)$ is K . This apparent paradox is completely analogous to that of light passing through a dielectric medium. Light has a certain wavelength in free space which differs from that in the dielectric because the scattered waves added to the incident wave continually phase shift the incident wave, which has the free-space wavelength, to produce a combination wave with the different wavelength of the dielectric.

The fact that the potential around an impurity is different from the potential in between the impurity does not imply a spatially dependent band structure. The states ψ_q that we are considering are eigenstates of the system and their energies are the same independent of position. What does vary is the form of ψ_q . In the perfectly periodic potential case, the wave function is the same in each unit cell up to a phase factor. In the case of an alloy, ψ_q has a different form near an impurity than in between, but such a difference does not lead to a spatially dependent band structure.

To recapitulate the preceding discussion, we have associated three different wave vectors with the alloy wave function of energy $E_0(q)$. One is the wave vector \mathbf{q} which is the solution of the Schrödinger equation of energy $E_0(q)$ in between the impurities where the alloy appears like the pure metal. Another is the wave vector \mathbf{K} which is the wave vector of the coherent part of the wave function and its relation to \mathbf{q} is given by Eq. (8). The third is the rigid-band-model wave vector \mathbf{k} whose relation to \mathbf{q} we have not yet determined. To determine this we must determine $E(k)$, the real part of the energy of the adiabatically corresponding state in the alloy. In our dilute case $\Delta E(k) = E(k) - E_0(k)$ will be proportional to $n\alpha$, the number of impurities per unit volume. The coefficient of proportionality can be determined in

the special case of a single impurity. Consider a single impurity placed at the center of a sphere of the pure metal of radius R . The impurity potential V_0 introduces phase shifts $\delta_l(k)$ into the various angular-momentum states of the electron with wave number k . In order to match the boundary conditions, a state of angular momentum l in the pure metal with wave number k is changed adiabatically to k' , where

$$kR = k'R + \delta_l(k). \quad (11)$$

Remembering that far enough away from the impurity, the potential seen by an electron is exactly the same as in the pure metal, and thus the same energy-versus-wave-number relationship holds in the alloy as in the pure metal in this region, we have

$$\Delta E_l(k) = E_0(k') - E_0(k) \approx \frac{\hbar^2 k}{m} (k' - k) = -\frac{\hbar^2 k}{m} \frac{\delta_l(k)}{R}, \quad (12)$$

where $\Delta E_l(k)$ is the change in energy of the state of angular momentum l . However, we are interested in $\Delta E'(k)$, the change in energy of a plane-wave state caused by a single impurity. Since this plane-wave state is composed of all angular-momentum states weighted by their degeneracy, we can determine $\Delta E'(k)$ by

$$\begin{aligned} \Delta E'(k) &= \sum_l \Delta E_l(k) (2l+1) / \sum_l (2l+1) \\ &= -\frac{\hbar^2 k}{mR} \sum_l \delta_l (2l+1) / \sum_l (2l+1). \end{aligned} \quad (13)$$

For a finite volume the denominator of (13) is finite because the maximum value of l is limited. For a spherical sample of radius R , the maximum value that an electron can have and still remain inside the sample is approximately $l = kR$. Using the relationship that $\rho_0(E_0)$, the density of states of the pure metal at $E_0(k)$ per unit volume, is given by

$$\frac{4}{3}\pi R^3 \rho_0(E_0) = \frac{R}{\hbar^2} \frac{2m}{\pi k} \sum_l (2l+1), \quad (14)$$

we can write (13) as

$$\Delta E'(k) = -\frac{2}{\pi} \sum_l \delta_l (2l+1) / \frac{4}{3}\pi R^3 \rho_0(E_0). \quad (15)$$

The number of impurities per unit volume in this case is $[(4\pi/3)R^3]^{-1}$. For $n\alpha$ impurities per unit volume $\Delta E(k)$ is

$$\Delta E(k) = -\frac{2n\alpha}{\pi} \sum_l \delta_l (2l+1) / \rho_0(E_0). \quad (16)$$

We then have the relationship between k and q that

$$E(k) = E_0(q), \quad (17)$$

and from the definition of $\Delta E(k)$ and (17) we obtain

$$k^2 = q^2 + \frac{4mn\alpha}{\hbar^2 \pi} \sum_l \delta_l (2l+1) / \rho_0(E_0). \quad (18)$$

Using the relationship that

$$\rho_0(E_0) = km / \pi^2 \hbar^2, \quad (19)$$

Eq. (18) can be written as

$$k^2 = q^2 + \frac{4\pi n\alpha}{k} \sum_l \delta_l (2l+1). \quad (20)$$

Using (8), (9), and (20) we can obtain the relationship between k and K to be

$$k^2 = K^2 + \frac{4\pi n\alpha}{k} \sum_l (2l+1) (\delta_l - e^{i\delta_l} \sin \delta_l). \quad (21)$$

It is important to keep clear the distinction between the adiabatic and the dielectric corresponding states. In the adiabatic case a current-carrying eigenstate of the pure metal of a given energy is transformed into χ , a current-carrying state of the alloy but with a finite lifetime and a differing energy. In the dielectric case a current-carrying eigenstate of the pure metal of a given energy is transformed to a non-current-carrying eigenstate ψ of the alloy of the same energy. What we now show is that, at least to order α , the states ψ and χ are closely related to another. In fact, the χ which has a given real part of the energy $E(k)$ is ψ of energy $E(k)$ with the imaginary part of K set equal to zero. To show this we show that the energy of the ψ with the imaginary part of K set to zero is complex and equal to that of χ . We know that the energy of ψ can be written as a function of K ,

$$E(K) = E_0(q), \quad (22)$$

where K is complex and can be written in terms of its real and imaginary parts as

$$K = K_1 + iK_2. \quad (23)$$

Now if $K_2 = 0$, then the energy becomes complex and to first order in α ,

$$E(K_1) = E_0(q) - iK_2 E'(K_1), \quad (24)$$

where $E'(K_1) = |\nabla_{K_1} E(K_1)|$.

The imaginary part of the energy of χ , which we have denoted by $\frac{1}{2}\Gamma$, can be obtained by reasoning similar to that used to determine $E(k)$. We first find the imaginary part of the energy for a single impurity by calculating the total scattering cross section, and multiply by the number of impurities to find Γ . By use of the optical theorem of scattering theory,⁸ we find

$$\frac{1}{2}\Gamma = \frac{2\pi n\alpha \hbar^2}{m} \text{Im} f_0, \quad (25)$$

⁸ Reference 6, p. 183.

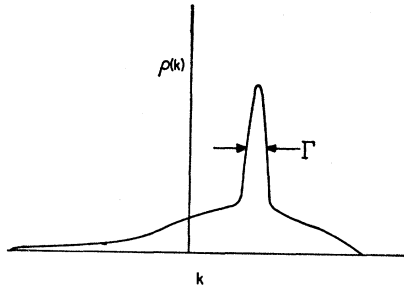


FIG. 1. The distribution of wave number in an eigenstate for the model of a dilute alloy. The width of the peak Γ is proportional to α , the fractional amount of impurity. The height of the broad distribution is proportional to α while its width remains fixed.

where $\text{Im}f_0$ means the imaginary part of f_0 . Comparison with (24) and (8) shows that to first order in α

$$\frac{1}{2}\Gamma = K_2 E'(K_1). \quad (26)$$

Thus we have proved the desired relation between χ_k and ψ_q .

Some further clarification of the relation between χ_k and ψ_q is in order. The eigenstate ψ_q represents the steady state of an incoming electron suffering both real transitions into other states and virtual transitions representing modifications of the incoming state in the vicinity of the impurities and a change in wave number. The noneigenstate χ_k represents a plane-wave state initially created throughout the whole alloy. The alloy introduces virtual transition modifications into χ_k , but the real transitions do not modify it; they only produce the finite lifetime of the state. In ψ_q the decay in real space of its coherent part is accounted for by the creation of states into which the incoming electron can make real transitions. In χ_k these real transitions are not included in the spatial variation of χ_k but in its time dependence as a finite lifetime.

Equation (21) indicates that the rigid-band-model wave number of a state and the real part of the actual wave number differ by order δ^2 and thus of order V_0^3 . This indicates that the rigid-band-model description of the Fermi surface is valid to second order in V_0 .

III. POSITRON ANNIHILATION IN ALLOYS

There are two different types of positron-annihilation experiments used to study the properties of solids. One measures the angular distribution of the annihilation γ rays for the two- γ -ray decay mode.⁹ This determines the distribution of the solid's electron momentum components perpendicular to the direction of the γ rays. The other measures the intensity of the annihilation γ rays emitted exactly antiparallel to one another as a

function of the orientation of the single-crystal sample.¹⁰ Assuming that the core effects can be taken into account, the intensity is assumed to be proportional to the dimensions of the Fermi surface in the direction of the observed γ rays passing through the k -space origin.

In this section we analyze the momentum distribution of the alloy wave function in order to interpret positron-annihilation experiments in alloys. Inspection of the wave function in (10) indicates that there are two distinct contributions to the momentum. One is the term $e^{i\mathbf{K}\cdot\mathbf{r}}$ which in view of the complex value of \mathbf{K} gives a momentum distribution peaked at \mathbf{K}_1 with a width of order of \mathbf{K}_2 , i.e., proportional to α . This momentum width comes from real transitions from the state χ_k to other states $\chi_{k'}$. The other contribution comes from the last term in Eq. (10) and represents virtual and real transitions. The virtual transitions give a broad distribution whose width is constant but whose magnitude is proportional to α . This is illustrated in Fig. 1. In an experiment, only the first contribution—the momentum peak—will be observable; the broad distribution will blend into the background. Thus momentum-measuring experiments measure K_F , where, by Eq. (8),

$$K_F^2 = q_F^2 + 4\pi n\alpha f_0. \quad (27)$$

Here q_F is the Fermi wave number of the pure metal assuming no volume change on alloying. The area under the peak is now less than 1 for a given electron state because the total area in Fig. 1 should be equal to 1. This decrease in the peak area is sometimes referred to as a renormalization of the wave function. To calculate this renormalization we calculate the area outside of the peak. The second term in Eq. (10) contains real scattered waves at the energy of the incident wave and virtual scattered waves which are composed of unperturbed states of energies different from the incident energy. The real scattered waves in the forward direction change q to K . The real scattered waves in the other directions do *not* decrease the weight of the peak because they just redistribute the \mathbf{K} of energy E into other directions. This redistribution is compensated by the scattering from other states of the same energy into the \mathbf{K} state. The decrease in the weight of the peak comes from only the virtual transitions. To calculate the weight in the virtual transitions we expect that for dilute alloys this weight will be proportional to the number of impurities $n\alpha$. The constant of proportionality is determined by considering the case of a single impurity in a free-electron gas of volume V . The wave function in that case is given by (6), where G_0 can be written as

$$G_0(\mathbf{r}, \mathbf{r}') = \frac{1}{V} \int \frac{e^{i\mathbf{k}\cdot(\mathbf{r}'-\mathbf{r})}}{[E_0(q) - E_0(k)]} \frac{d^3k}{(2\pi)^3}. \quad (28)$$

⁹ P. R. Wallace, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10.

¹⁰ D. L. Williams, P. Petyevitch, and G. Jones, *Bull. Am. Phys. Soc.* **10**, 1181 (1965); O. Sueoka, *J. Phys. Soc. Japan* **23**, 1246 (1967).

If we normalize ψ_q to one per unit volume, the total weight in ψ_q of wave numbers other than \mathbf{q} is given by

$$B_1^2 = \frac{1}{V^2} \sum_{k \neq q} \left| \frac{\int e^{-i\mathbf{k}\cdot\mathbf{r}'} V(\mathbf{r}') \psi_q(\mathbf{r}') d^3r'}{E_0(q) - E_0(k)} \right|^2$$

$$= \frac{2}{V} \frac{\partial}{\partial E_0(q)} \left\{ P \int \frac{d^3k}{(2\pi)^3} \frac{|\int e^{-i\mathbf{k}\cdot\mathbf{r}'} V(\mathbf{r}') \psi_q(\mathbf{r}') d^3r'}{E_0(k) - E_0(q)} \right\}, \quad (29)$$

where P denotes principle value and $\partial/\partial E_0(q)$ is taken holding \mathbf{q} fixed. Using the definition of the t matrix

$$t\phi_q = V(\mathbf{r})\psi_q, \quad (30)$$

we can write (29) also as

$$B_1^2 = \frac{1}{V} \frac{\partial}{\partial E_0(q)} \Sigma(E_0(q), \mathbf{q}), \quad (31)$$

where

$$\Sigma(E_0(q), \mathbf{q}) = P \int \frac{d^3k}{(2\pi)^3} \frac{|t_{k\mathbf{q}}|^2}{(E_0(k) - E_0(q))},$$

and

$$t_{k\mathbf{q}} = \int e^{-i\mathbf{k}\cdot\mathbf{r}} V(\mathbf{r}) \psi_q(\mathbf{r}) d^3r.$$

In the case considered, the number of impurities per unit volume is $1/V$. Thus for $n\alpha$ impurities per unit volume (31) becomes

$$B^2 = n\alpha \frac{\partial}{\partial E_0(q)} \Sigma(E_0(q), \mathbf{q}). \quad (32)$$

In Fig. 1, B^2 represents the area in the broad distribution. The weight associated with the peak in the momentum distribution of Fig. 1 is

$$1 - B^2(E_0(q)) = 1 - n\alpha \frac{\partial}{\partial E_0(q)} \Sigma(E_0(q), \mathbf{q}). \quad (33)$$

The momentum distribution in the ground state of the alloy can be obtained by integrating the contribution from each state over the total number of occupied states. To order α , the number of occupied states ψ_q per unit energy at the vector \mathbf{q} of energy $E_0(q)$ is given by^{4,11}

$$N(E_0(q)) = f(E_0(q)) \rho_k(E_0(q)), \quad (34)$$

where

$$f(E_0(q)) = [1 - e^{-(E_F - E_0(q))/kT}]^{-1},$$

$$\rho_k(E_0(q)) = \frac{2}{(2\pi)^3} \int \frac{dS_k}{|\nabla_k(E_0(q))|}, \quad (35)$$

and k is the rigid-band wave number corresponding to q which is given by (20). The expression on the right side of (35) is evaluated in the rigid-band-model k space

¹¹ E. A. Stern, Phys. Rev. 144, 545 (1966).

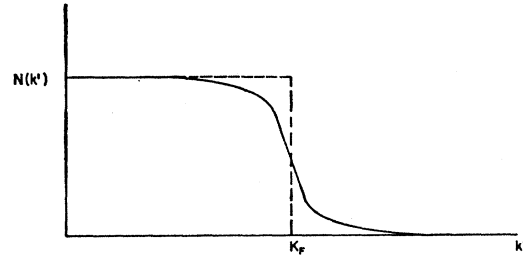


FIG. 2. The distribution of wave number $N(k')$ in a dilute alloy. The dashed line is for a pure metal with the same Fermi wave number.

where dS_k is an elemental area on the constant energy surface $E = E_0(q)$ in the k space. Note that the right side of (35) does not use q or K space. The validity of this result is discussed in Refs. 4 and 11 and it can briefly be summarized as follows: There is a one-to-one correspondence between the rigid-band-model states and those of the alloy via the adiabatic correspondence discussed in the previous section. The adiabatic alloy states χ_k are not eigenstates but have an imaginary part to their energy. However, the real part of their energy is the same as that of the true eigenstates and the imaginary part of their energy contributes to $\rho(E)$ of order α^2 . Thus to order α the imaginary energy part can be neglected and the χ_k can be treated as eigenstates. Because of their one-to-one correspondence to the rigid-band states their number can be counted in k space, thus leading to Eq. (35).

Putting all of these ideas together the momentum distribution in the alloy $N(k')$ is given by

$$N(k') = \frac{2}{\pi^3} \int [1 - B^2(E_0(q))] f(E_0(q))$$

$$\times \prod_i \frac{K_{2i}}{[(K_{1i} - k_i')^2 + K_{2i}^2]} \frac{dS_k dE_0(q)}{|\nabla_k E_0(q)|}$$

$$+ \frac{2}{(2\pi)^3} \frac{\partial}{\partial E_0(k')}$$

$$\times \left\{ P \int \frac{|t_{k'\mathbf{q}}|^2 f(E_0(q)) dS_k dE_0(q)}{[E_0(q) - E_0(k')] |\nabla_k E_0(q)|} \right\}. \quad (36)$$

The first integral on the right side of Eq. (36) represents the contribution from the coherent parts of the wave function, the peak contributions. The product \prod_i means the product where i has the three values x, y, z corresponding to the three components of $\mathbf{K} = \mathbf{K}_1 + i\mathbf{K}_2$. The second integral on the right side of (36) represents the contributions from the virtual transitions in ψ_q , the broad background in Fig. 1. Schematically, one expects the $N(k')$, where k' is now the magnitude of k' , to look as shown in Fig. 2. For small values of k' , $N(k') \approx 1$ because the width of the broad background is of the order of K_F . Then the second integral in (36) is approx-

imately equal to $B^2(E_0(k'))$ and makes $N(k') \approx 1$. As we increase k' and approach K_F so that $K_F - k'$ becomes smaller than the width of the broad background, the contribution from the second integral on the right side of (36) becomes less than $B^2(E_0(k'))$, and $N(k') < 1$. If K_{2F} were zero, then the slope of $N(k')$ at K_F would be infinite. However, because $K_{2F} \neq 0$, we end up with a finite slope at K_F . Also, because of the broad background, we obtain the tail in $N(k')$ for $k' > K_F$.

Angular correlation positron-annihilation experiments by Stewart on LiMg alloys¹² indicate a momentum distribution as shown in Fig. 2. In pure Li the positron data is consistent with a rectangular momentum distribution as indicated by the dashed lines in Fig. 2. In the LiMg alloys, the positron data indicate a momentum distribution that drops below the dashed lines below the Fermi momentum, in agreement with Fig. 2. Stewart correctly attributed such behavior in the alloy to the virtual transitions corresponding to the relative pileup of charge around the Mg ions. The calculation in this paper completely confirms the suggestion of Stewart.

The positron-annihilation experiments that use a rotating single-crystal sample to measure the dimensions of the Fermi surface must account for the effect of the renormalization of the electron wave function. If not correctly accounted for, this renormalization effect would appear as a decrease in the Fermi-surface dimension with alloying. If the renormalization were independent of sample orientation, it would not change the relative shape of the Fermi surface and could be accounted for by renormalizing the experimental data. However, if the Fermi surface is anisotropic, one would expect in general that the renormalization would also be anisotropic, and the Fermi-surface shape determined by the rotating-crystal method of positron annihilation would give an incorrect shape.

Another experiment that has been used to determine the size of Fermi surfaces in alloys is to determine the Kohn anomaly in the phonon spectrum measured by neutron scattering.^{13,14} Such a measurement determines the Fermi-surface size in K space, just as positron-annihilation experiments do. One expects deviations from the rigid-band model, then, when the alloy cannot be treated by perturbation theory. The situation when perturbation theory is expected to be or not be valid is discussed in Ref. 11.

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IV. SUMMARY

The properties of electron states in a model alloy is considered. The model consists of a free-electron gas with a dilute number of impurities. The alloy states differ from the free-electron states in two ways: (1) Because of a localization of charge around the impurities, which is described by virtual transitions, a broad momentum distribution is added to the alloy state whose weight is proportional to the concentration of impurities. (2) In addition to the broad background, the coherent part of the state contributes a peak in the momentum distribution about a value K_1 , the real part of K given by Eq. (8). The width of the peak is $2K_2$, the imaginary part of K . The width of this peak comes physically from the scattering of free-electron states by the impurities and corresponds to a blurring of the Fermi surface for states at the Fermi energy. Besides the smearing of the peak the impurities also shift the value of the peak in an analogous manner to a dielectric medium. The relationship between the wave number K in the alloy, the rigid-band model wave number k , and the wave number q that a free-electron of the same energy has, is discussed in detail. In particular K and k differ when second-order perturbation theory is no longer valid for the alloy.

Because of the broad background, a renormalization occurs for the coherent part of the wave function, giving it less weight than 1. This renormalization contributes important effects in positron-annihilation experiments and must be included in order to correctly interpret the results in alloys.

Note added in proof. It is important to distinguish between the discussion in this paper on the decrease of the weight in the momentum distribution near K_F and the variation of the positron-annihilation probability in pure metals as a function of the k state of the electron.^{15,16} The variation discussed in this paper is caused by alloying and is an additional mechanism to the one producing the variation in pure metals.

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