

Electron Density of States of Dilute Alloys*

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The change in the electron density of states with dilute alloying is directly related to the shielding of the added impurities. If there is no volume change on alloying, the change in $\rho(E)$, the density of states at energy E , is proportional to the excess charge attracted to the impurities from the electron states of energy E . The low-temperature electronic specific heat of various dilute alloys can be interpreted in this manner to obtain the shielding contribution of the electrons at the Fermi energy. The rigid-band model has no obvious relationship to the electronic specific heat of dilute alloys even if the specific heat depends only on the electron-per-atom ratio. Such a dependence means only that the attracted charge is proportional to the valence difference between the impurity and the host, a result expected from linear response theory.

I. INTRODUCTION

HISTORICALLY, one of the main motivations for measuring the low-temperature electronic specific heat of dilute alloys was to discover the variation of the density of states of the pure host as a function of energy.¹⁻¹³ The incorrect reasoning used was based on the rigid-band model which assumed that the density of states curve $\rho(E)$ of the pure host remained unchanged with alloying. If alloying changed the electron-per-atom ratio \bar{z} , the Fermi surface would expand or contract to accommodate the varying number of electrons. Since the electronic specific heat measures the density of states at the Fermi energy, it would be possible to plot out the density-of-states curve of the pure host by appropriate alloying. When this model is applied to real alloys one runs into contradictions. The noble metals and their alloys give the simplest example of the contradiction. The band structure of the noble metals is well enough known^{14,15} to permit a prediction of the change of $\rho(E)$ with \bar{z} . Since the Fermi surface of the pure metals is touching the zone boundary, increasing the \bar{z} should decrease $\rho(E)$ if the rigid-band model were valid. Measurements indicate

just the opposite behavior, namely, an increase of $\rho(E)$ with increased \bar{z} . The obvious cause of this behavior is the breakdown of the rigid-band model,¹⁶ but there has not been a quantitative theory to explain the measured result.

In this paper we show that there is a relationship between the change in $\rho(E)$ on alloying and the shielding of the impurities by states near the Fermi energy. An increased $\rho(E)$ with the addition of dilute impurities indicates that the electronic states at the Fermi energy are attracted by the impurities and deposit more electronic charge in the vicinity of the impurities to help shield them. Since this is the expected behavior for impurities that increase \bar{z} , one expects, in general, an increase of $\rho(E)$ with increased \bar{z} more or less independently of the host. The experimental results for the noble-metal alloys are consistent with this picture.

The outline of the paper is the following: Section II proves the relationship between $\rho(E)$ and the shielding of the electron states at the energy E . Section III discusses the range of validity of this relationship. A discussion is presented in Sec. IV, and a summary and conclusion are given in Sec. V.

II. DENSITY OF STATES AND SHIELDING

In this section we assume that the Laue theorem¹⁷ is valid and use it to derive the relationship between shielding and $\rho(E)$. This theorem states that the particle density per unit energy range is approximately independent of the form of the boundary, at distances from the boundary greater than a characteristic particle wavelength at the energy considered. Consider the model of a solid composed of a host and a dilute number of substitutional impurities which do not vary the volume of the solid. By dilute we mean that the average distance between impurities is many times the size of the shielding cloud, so that to a good approximation there is no appreciable overlap of the shielding clouds of different impurities. We assume that the

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¹⁷ C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), pp. 339-341.

impurities are distributed throughout the solid in such a manner so that there is no appreciable clustering. Finally, we assume that the electron states can be determined by a single-particle Hamiltonian. Thus we neglect interactions between electrons except insofar as they contribute to the selfconsistent potential via shielding.

According to the Laue theorem, in the region away from the impurities,

$$\sigma_E^0(\mathbf{r})\rho^0(E) = \sigma_E(\mathbf{r})\rho(E), \quad (1)$$

where $\sigma_E(\mathbf{r})$ is the alloy particle density at \mathbf{r} per electron state of energy E , $\rho(E)$ is the alloy density of states at E , and the superscript 0 denotes the corresponding quantities in the pure host.

If the electron states of energy E contribute any shielding around the impurities, we have

$$\sigma_E(\mathbf{r}) \neq \sigma_E^0(\mathbf{r}). \quad (2)$$

This follows from the fact that the eigenstates are normalized to 1. Any increase or decrease of the electronic charge around the impurities due to shielding must produce the opposite change in electron density away from the impurities.

If the average excess charge at energy E attracted by each impurity is $(\delta\sigma_E)/V$, where V is the volume of the solid, we have

$$\sigma_E^0(\mathbf{r})/\sigma_E(\mathbf{r}) = 1/(1 - n\delta\sigma_E), \quad (3)$$

where n is the number of impurities per unit volume. Combining (1) and (3) gives

$$\begin{aligned} \rho(E) &= \rho^0(E)/(1 - n\delta\sigma_E), \\ &\approx \rho^0(E)(1 + n\delta\sigma_E). \end{aligned} \quad (4)$$

Physically, $(1 + n\delta\sigma_E)$ is the ratio of the total charge attracted around the impurities per unit volume to the total charge per unit volume contributed by states at energy E .

We check Eq. (4) by considering the free-electron gas as the host. In this model¹⁸ the excess charge attracted around a single impurity is $(1/R)(d\delta_l/dk)$ for a partial-wave state of wave number k and angular momentum l . Here δ_l is the phase shift introduced by the impurity for this partial wave and R is the radius of the spherical sample. The impurity, assumed to have a spherical potential, is placed in the center of the sphere to provide spherical symmetry. The average excess charge attracted by the impurity is obtained by summing the contribution from each (k, l) state at energy E and dividing by the total number of such states. By this means one obtains

$$\frac{\delta\sigma_E}{V} = \frac{2}{\pi} \sum_l \frac{(2l+1)\delta_l'}{\rho^0(E)h^2k}, \quad (5)$$

where $\delta_l' = d\delta_l/dk$ and m is the electron mass. Com-

binning (5) with (4), we obtain

$$\rho(E) = \rho^0(E) + \frac{2mnV}{\pi h^2k} \sum_l (2l+1)\delta_l'. \quad (6)$$

This agrees with the standard results for this model.¹⁹

III. RANGE OF VALIDITY

In order to derive the result in (4) relating $\rho(E)$ and the shielding charge $\delta\sigma_E$, it was necessary to assume the Laue theorem which asserts (1) in the region between impurities. We now analyze, using an argument due to Peierls,²⁰ the range of validity of (1).

Consider the Green's function of the alloy $G(\mathbf{r}t, \mathbf{r}'t')$ defined by

$$\left(\frac{-\hbar^2 \nabla^2}{2m} + V(\mathbf{r}) - \frac{i\hbar \partial}{\partial t} \right) G(\mathbf{r}t, \mathbf{r}'t') = -\delta(\mathbf{r} - \mathbf{r}')\delta(t - t'), \quad (7)$$

where $V(\mathbf{r})$ is the selfconsistent potential in the dilute alloy. Physically, $G(\mathbf{r}t, \mathbf{r}'t')$ describes the amplitude of finding an electron at \mathbf{r} and time t when a single electron is created at \mathbf{r}' at time t' . We set the boundary condition that $G(\mathbf{r}t, \mathbf{r}'t') = 0$ for $t < t'$. The solution for $G(\mathbf{r}t, \mathbf{r}'t')$ is

$$G(\mathbf{r}t, \mathbf{r}'t') = -i \sum_n \psi_n(\mathbf{r})\psi_n^*(\mathbf{r}')e^{-i\omega_n(t-t')}, \quad (8)$$

where $\psi_n(\mathbf{r})$ are the eigenstates of the alloy and $\hbar\omega_n$ are their eigen energies. The fourier transform $G_\omega(\mathbf{r}, \mathbf{r}')$ is defined by

$$\begin{aligned} G_\omega(\mathbf{r}, \mathbf{r}') &= \int_0^\infty G(\mathbf{r}t, \mathbf{r}'t')e^{i\omega(t-t')}d(t-t') \\ &= \lim_{s \rightarrow 0+} \sum_n \frac{\psi_n(\mathbf{r})\psi_n^*(\mathbf{r}')}{\omega - \omega_n + is}. \end{aligned} \quad (9)$$

We note that

$$-\frac{\hbar}{\pi} \text{Im} G_\omega(\mathbf{r}, \mathbf{r}) = \hbar \sum_n \psi_n(\mathbf{r})\psi_n^*(\mathbf{r})\delta(\omega - \omega_n) \quad (10)$$

and

$$-\frac{\hbar}{\pi} \text{Im} \int G_\omega(\mathbf{r}, \mathbf{r})d^3r = \hbar \sum_n \delta(\omega - \omega_n) = \rho(E), \quad (11)$$

where $E = \hbar\omega$, and the eigenstates are normalized to 1. Eq. (10) can conveniently be written as

$$-(\hbar/\pi) \text{Im} G_\omega(\mathbf{r}, \mathbf{r}) = \sigma_E(\mathbf{r})\rho(E), \quad (12)$$

where $\sigma_E(\mathbf{r})$ is the charge density per state at \mathbf{r} for the states with energy E .

In general, $G_\omega(\mathbf{r}, \mathbf{r})$ is affected by the presence of each impurity. In fact, we have the well-known relation²¹ relating $G_\omega(\mathbf{r}, \mathbf{r})$ and $G_\omega^0(\mathbf{r}, \mathbf{r})$, where $G_\omega^0(\mathbf{r}, \mathbf{r})$ is

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¹⁸ See, for example, Ref. 17, pp. 341-344.

the Green's function for the pure host with no impurities,

$$G_{\omega}(\mathbf{r}, \mathbf{r}) = G_{\omega}^0(\mathbf{r}, \mathbf{r}) + \int G_{\omega}^0(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') G_{\omega}(\mathbf{r}', \mathbf{r}) d^3r'. \quad (13)$$

However, in practice we are not really interested in $\rho(E)$ but some average of $\rho(E)$ over an energy interval ΔE which is small compared to the energies of interest. As pointed out by Peierls,²⁰ such a "fuzzed out" $\rho(E)$ can be obtained by taking the Fourier transform of $G(\mathbf{r}, \mathbf{r}', t)$ over only the time interval $\tau > t - t' > 0$, instead of the interval $\infty > t - t' > 0$ as previously.

This Fourier transform denoted by $G_{\omega}(\mathbf{r}, \mathbf{r}', \tau)$ has the property that

$$-(\hbar/\pi) \text{Im} G_{\omega}(\mathbf{r}, \mathbf{r}, \tau) = \sigma_E(\mathbf{r}, \tau) \rho(E, \tau), \quad (14)$$

where $\rho(E, \tau)$ and $\sigma_E(\mathbf{r}, \tau)$ are averaged over the interval $\Delta E \approx \hbar/\tau$. Now if \mathbf{r} is farther from any impurity than the distance $2v_E\tau$, then $\text{Im} G_{\omega}(\mathbf{r}, \mathbf{r}, \tau)$ is not affected by the impurities and has the same value as in the pure host. Here v_E is the maximum velocity of electrons of energy E . The invariance of $\text{Im} G_{\omega}(\mathbf{r}, \mathbf{r}, \tau)$ depends on $V(\mathbf{r})$ not changing on alloying. In that case, the differential equation which determines $G(\mathbf{r}, (t' + \tau); \mathbf{r}, t')$ in the vicinity of \mathbf{r} is exactly the same, with or without impurities. The disturbances introduced by the impurities have no opportunity to scatter back and affect the point \mathbf{r} in the time interval τ . Thus,

$$\sigma_E^0(\mathbf{r}, \tau) \rho^0(E, \tau) = \sigma_E(\mathbf{r}, \tau) \rho(E, \tau), \quad (15)$$

where the superscript 0 denotes the corresponding quantities in the pure host.

To complete the proof of (15), we must show that $V(\mathbf{r})$ does not change on alloying. This follows from (15) itself, which states that the alloy electronic charge density of energy E averaged over an energy interval \hbar/τ has exactly the same magnitude and spatial dependence as in the pure host. The potential $V(\mathbf{r})$ is composed of the ion core potential plus the field of the conduction electron density. Since both of these are the same in the alloy and in the pure host, $V(\mathbf{r})$ remains unchanged in alloying.

We now estimate the value of τ that enters in practice. The determining requirement is that $\rho(E, \tau)$ closely approximates $\rho(E)$. This will be the case when over the energy interval \hbar/τ , $d\rho(E)/dE$ does not change appreciably. Typically in metals, $\rho(E)$ and $d\rho/dE$ have appreciable variations for energy changes of the order of the bandwidth—of the order of several eV. Thus for $\hbar/\tau \lesssim 0.2$ eV we would expect that $\rho(E, \tau)$ closely approximates $\rho(E)$, except when $\rho(E)$ has a van Hove type of singularity at E .

From Eq. (4) we note that in the dilute limit the change in $\rho(E)$ is proportional to n , the number of impurities per unit volume. In practice, the range of validity of the arguments presented here can be determined from the experimental measurements by de-

termining the concentration region in which the change in $\rho(E)$ remains linear with concentration. The estimate in the above paragraph plus the definition of τ given below Eq. (14) leads to the conclusion that the change in $\rho(E)$ should remain linear until an impurity concentration of the order of several %.

IV. DISCUSSION

We now proceed to analyze specific-heat measurements on dilute alloys in the context of the presentation in the previous sections. The connection between the shielding of the impurities and the change in density of states gives a straightforward explanation of the experimental data. One is not measuring the variation of the $\rho(E)$ of the host material with varying β , nor is one measuring directly any electron-phonon enhancement factor variations. One is simply measuring the amount of charge attracted to the impurities for the electron states at the Fermi energy. Electron-phonon interactions or any other effect can contribute only in how they influence this shielding charge around the impurities. The results of Dicke and Green¹⁰ on Al-based alloys which indicate a decrease of $\rho(E_F)$ with Zn impurities, and an increase with Ge impurities indicate that the electron states at E_F are repelled from the Zn impurities and attracted to the Ge impurities. This is precisely what one expects from usual shielding considerations using perturbation theory. Interpreting these results in terms of Eq. (4), one finds that the electrons at the Fermi energy deposit 0.6 as much charge on Zn atoms and 1.4 times as much charge on Ge atoms as deposited on the Al atoms. The effect on $\rho(E_F)$ of volume changes on alloying as estimated from a free-electron model are unimportant.

In the noble-metal alloys, there are indications that the volume changes on alloying contribute appreciably

TABLE I. Charge from electrons at E_F attracted around dilute impurities as determined from low-temperature electron specific heat data. Here γ is the coefficient of the linear temperature term of the specific heat and x is the atomic fraction of the impurity. The corrected values in the third column use the volume corrections of Ref. 4 applied to the Cu- and Ag-based alloys. The volume corrections for the Al-based alloys are estimated by the free-electron model. The last column gives the ratio of the charge at E_F attracted around an impurity to that around the host atom. The host atom is italicized in the first column.

Alloy	$d \ln \gamma / dx$	$(d \ln \gamma / dx)_{\text{corrected}}$	$\sigma_{\text{imp}} / \sigma_{\text{host}}$
<i>Al</i> Ge	0.37 ^a	0.4	1.4
<i>Al</i> Zn	-0.37 ^a	-0.4	0.6
<i>Cu</i> Sn	0.72 ^b	0.9	1.9
<i>Cu</i> Zn	0.3 ^c	0.5	1.5
<i>Ag</i> Cd	0.27 ^d	0.45	1.45
<i>Ag</i> Zn	0.65 ^e	0.45	1.45
<i>Ag</i> Sn	0.66 ^f	1.1	2.1
<i>Ag</i> Au	-0.06 ^g	-0.06	0.94
<i>Au</i> Ag	-0.22 ^g	-0.22	0.78

^a Reference 10.

^b Reference 1.

^c References 1 and 2.

^d Reference 8.

^e Reference 4.

^f Reference 3.

^g Reference 23.

to the changes in the low-temperature electronic specific heat. Since the theory presented in this paper assumed no volume variation on alloying, the changes in $\rho(E)$ produced by volume changes must be corrected for. In doing this we follow the analysis of Green⁴ on Ag-rich alloys and assume that the same volume corrections can be used, not only on Ag-rich alloys, but also on Cu-rich alloys. The data are summarized in Table I, which also includes the Al data. We note the offhand surprising result that Pd impurities attract more charge at E_F than do the host Ag atoms. Perturbation theory of shielding applied to the free-electron model predicts the opposite behavior. However, a model which can explain this is one which treats the Pd impurity as a virtual bound state²² located in the vicinity of the Fermi energy, so that the electrons can resonate with it at that energy.

Also included in Table I is an analysis of the Ag-Au alloy system. In this system there are appreciable decreases in $\rho(E_F)$ at both the Ag-rich and Au-rich ends,^{7,23} and the volume changes are negligible.²⁴ The variation of $\rho(E)$ with alloying agrees with that predicted by perturbation theory.²⁵ Although both Ag and Au have the same valence, there is a net charge transfer between them at E_F . Of course, the net charge transfer between them integrated over all energies must be zero by charge neutrality. Thus, the fact that in the gold-rich alloys the Au atoms attract more charge at E_F than the dilute Ag impurities implies that at some lower energy the reverse is true.

We do not extend our analysis to the extensive data on the transition-metal alloys.¹¹⁻¹³ In such alloys long-range magnetic effects can occur which invalidate the present analysis. In addition, it would take careful analysis to subtract out volume effects.

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²³ D. L. Martin, *Phys. Rev.* **176**, 790 (1968).

²⁴ W. B. Pearson, *Handbook of Lattice Spacings and Structure of Metals and Alloys* (Pergamon Press, Inc., New York, 1968), Vol. 1, p. 268.

²⁵ E. A. Stern, *Phys. Rev.* **144**, 545 (1966).

V. SUMMARY AND CONCLUSIONS

The changes in the low-temperature electronic specific heat of dilute alloys give information on the properties of the alloy and not directly on those of the host. In particular, these specific heat changes are directly related to the electronic charge at E_F attracted around the impurity. This explains why attempts to understand specific-heat data of dilute alloys in terms of the rigid-band model have so often been unsuccessful. On the other hand, the shielding of impurities must depend in some manner on the electronic structure of the host, so that there should be some indirect connection between the specific heat of dilute alloys and the host properties.

The experimental proof of the validity of the rigid-band model that is usually given is that the electron specific heat depends on only \mathfrak{z} and not the type of impurity. Thus, for example, if alloys of CuSn and CuZn produce the same specific-heat changes as a function of \mathfrak{z} , one would assume that the rigid-band model is valid. The analysis of this paper indicates that such a conclusion does not follow. The dependence of specific-heat changes on only \mathfrak{z} means that the amount of charge attracted to impurities is proportional to Z , the difference in valence between the host and the impurity. This is the case in linear response theory. Thus the correct conclusion to draw from the experimental dependence of the changes in $\rho(E_F)$ on only \mathfrak{z} is that the shielding can be treated by linear response theory, and not that the rigid-band model is correct.

It is estimated that up to several % of impurity concentration the changes in $\rho(E)$ vary linearly with concentration. It is in this range that the relationship between $\rho(E)$ and shielding applies.

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