PHYSICAL REVIEW B VOLUME 8, NUMBER 6 15 SEPTEMBER 1973

Electronic Density of States in Cu-Based Alloys*

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(Received 14 February 1973)

A detailed theoretical investigation has been made of the manner in which the electronic density of states of copper changes with the introduction of dilute nonmagnetic impurities. The formalism used is exact for a single impurity in a system of muffin-tin potentials, and takes into account the detailed character of the host band structure. The impurity potential is calculated through a self-consistent procedure utilizing a generalized Friedel sum rule. The results show a marked difference from the predictions of the rigid-band model. We find that the changes in the single-particle electronic density of states are not sufficient to account for the measured changes in the linear component of the specific heat. But due to the comprehensive nature of the calculations, it is possible to conclude that the discrepancy is due to other physical effects.

I. INTRODUCTION

The electronic structure of dilute copper (and other noble-metal-based) alloys have attracted considerable interest during recent years.[1-10] The primary experimental tool has been measurement of the coefficient of the linear term in the electronic specific heat, a quantity which in the independent-particle approximation (IPA) is directly proportional to the electronic density of states. The object of primary interest in the early experimental studies on the alloys was in fact the pure host material, since it was thought, on the basis of the rigid-band model,[11,12] that the density of states in the alloys would be closely related to that of the host. In particular, the rigid-band model predicts that the change in the electronic density of states, as a function of the concentration of impurities in the alloy, would be proportional to the energy derivative of the host density of states, evaluated at the Fermi level of the pure material.

It is well known that even the sign of the rigid-band prediction is frequently not in agreement with experiment. The coefficient γ of the linear term in the specific heat increases upon alloying of small amounts of polyvalent impurities with Cu, whereas the electronic density of states in Cu is a decreasing function of energy in the vicinity of the Fermi level.[13,14] Several authors[15-18] have attempted to go beyond a rigid-band model of these alloys. Jones,[15] Dawber,[16] and Haga[18] have attempted to construct more detailed theories of the electronic properties of these alloys. They argue that the density of states could be increased by impurity scattering. If the density of states in the pure metal has special features (e.g., a peak) lying below the Fermi surface, these features will not affect the low-temperature electronic specific heat of the pure metal, but they could affect that of the dilute alloy because of the smearing effect produced by impurity-induced scattering.

Jones[15] and Dawber[16] noted that there was a hump in the density of states just below the Fermi energy, which exists in noble metals where the energy surface first touches the edge of the first Brillouin zone. They both used a nearly-free-electron model for the energy bands and density of states, and completely neglected the *d* band. The free-electron basis of the Jones and Dawber calculations can be strongly criticized, since Cu is known to have significant *d* character at the Fermi surface.

Haga,[18] on the other hand, completely neglected the critical points in the Cu band structure that were the motivation behind the calculation of Jones and Dawber and assumed that the effect of impurity scattering was to broaden the *d* band, thereby increasing the density of states at the Fermi level. In his model the half-width of the broadened *d* band was left as an adjustable parameter, which was then fit to the data. No attempt was made to derive the value of this parameter from first principles.

It is quite possible that no independent-particle model will be able to account for the data. In normal metals it is known that γ is proportional to $(1+\lambda)\rho(E_F)$, where $\rho(E_F)$ is the band density of states at the Fermi energy and λ is the many-body enhancement factor. For copper the enhancement is of the order of 18%.[19] It is now apparent that there are at least two effects to be considered; the change in the enhancement due to alloy[20,21] and the change in the band density of states. This now makes the interpretation of measured changes in specific heat more difficult, since it is not possible to separate the two effects. On the other hand, an accurate calculation of either effect would help to clarify the issue.

The purpose of the work described in this paper is to make a quantitatively accurate calculation of the change in the electronic spectrum upon the addition of dilute amounts of impurities to copper. To do this we make a model of the alloy which, while necessarily approximate to facilitate calculation, does appear to contain the essence of the problem. The unperturbed host is treated in the muffin-tin approximation, which is certainly adequate for cubic materials like Cu. The introduction of the impurity is assumed to perturb the crystalline potential only within the muffin-tin sphere, which is centered on the impurity site. The calculation is then exact within this framework; in particular the complicated band structure of the host is fully incorporated into the calculations.

The structure of the paper is as follows: The relevant formalism is developed in Sec. II, which is followed by a discussion in Sec. III of the principle computations and in Sec. IV by a discussion of the representation of the impurity potential. Sections V and VI are concerned with our results for various Cu-based alloys and how they relate to specific-heat data.

II. FORMALISM

In this section of the paper we develop a set of relatively simple formulas which will allow us to calculate the difference between the electronic density of states in the alloy and the perfect-host material. The calculation proceeds in the following way. Let G be the Green's function (operator) for the perfect host, and $\mathcal{G}$ the analogous quantity for the alloy. As was discussed in Sec. I, in our model the crystalline potential in the host and alloy differ only within a spherical region of radius R surrounding the impurity. If $\Delta\rho(E)$ is the difference between the alloy and host density of states at energy E, then

$$\Delta\rho(E) = (2/\pi)\,\mathrm{Im}\,\mathrm{Tr}(\mathcal{G} - G).$$

Using

$$\mathcal{G} = G + GV\mathcal{G},$$

where V is the perturbation, leads to

$$\begin{aligned}\Delta\rho &= \frac{2}{\pi}\,\mathrm{Im}\,\mathrm{Tr}\,GV(1-GV)^{-1}G\\ &= -\frac{2}{\pi}\,\mathrm{Im}\,\mathrm{Tr}\,\frac{\partial G}{\partial E}\,V(1-GV)^{-1},\end{aligned}$$

where we have used the relation

$$\int \langle \bar{x}|\,G\,|\bar{y}\rangle\langle \bar{y}'|\,G\,|\bar{x}\rangle\, d\bar{x} = -\left\langle \bar{y}'\left|\,\frac{\partial G}{\partial E}\,\right|\bar{y}\right\rangle \,.$$

The prefactor of 2 arises from a summation over spin degrees of freedom. The last expression for $\Delta\rho$ can be written symbolically as

$$\Delta\rho = \frac{2}{\pi}\,\mathrm{Im}\,\mathrm{Tr}\,\frac{d}{dE}\,\ln(1-GV),$$

which stands for the equation

$$\Delta\rho = \frac{2}{\pi}\,\mathrm{Im}\,\frac{d}{dE}\sum_i \ln(\mu_i), \qquad (2.1)$$

where the numbers μ_i are the eigenvalues of the operator $1-GV$. For the appropriate choice of the branch of the logarithm the quantity

$$\Delta Z(E) = \frac{2}{\pi}\,\mathrm{Im}\sum_i \ln(\mu_i) \qquad (2.2)$$

is the difference between the total number of states in the interval $[-\infty, E]$ in the alloy and the host material.

The easiest way to evaluate this expression is to recognize that the central-cell potential in the host (which is replaced by the impurity when the alloy is formed) and the impurity potential in the alloy can be replaced by the energy-dependent δ-shell potentials introduced previously.[22] The total number of states in a finite energy interval is, by definition of the amplitudes of the δ-shell potentials, the same in some actual system and in a hypothetical system in which some or all of the spherical potentials are replaced by the δ shells. Furthermore, the Green's functions are identical in both systems for values of their arguments exterior to the region of the potential.[23] Using the notation of Ref. 23, the host and impurity δ-shell potentials take the form

$$V_\alpha = R^2 \sum_L \chi_L(\vec{r})(\gamma_{\alpha,l} - \gamma_{0,l})\chi_L(\vec{r}\,'),$$

where $\alpha = (i, h)$ for the impurity and host, respectively, and $\gamma_{\alpha,l}$ is the exact logarithmic derivative for the potential in question. The δ-shell potential representing the perturbation is therefore

$$V = R^2 \sum_L \chi_L(\vec{r})(\gamma_{i,l} - \gamma_{h,l})\chi_L(\vec{r}\,').$$

Now let $\phi(\vec{r})$ be an eigenfunction of $1-GV$ and μ the associated eigenvalue. The eigenvalue equation takes the form

$$(\mu-1)\phi(\vec{r}) = -\sum_L \langle\vec{r}\,|\,G\,|\,L\rangle V_l \phi_L,$$

where

$$\begin{aligned}&V_l = R^2(\gamma_{i,l} - \gamma_{h,l}),\\ &\phi_L = \int \chi_L(\vec{r})\,\phi(\vec{r})\,d\vec{r}\,,\\ &\langle\vec{r}\,|\,G\,|\,L\rangle = \int \langle\vec{r}\,|\,G\,|\,\vec{r}\,'\rangle\chi_L(\vec{r}\,')\,d\vec{r}\,'.\end{aligned}$$

Multiplying by $\chi_{L'}(\vec{r})$ and integrating leads to the algebraic eigenvalue equation

$$\sum_{L'} (\delta_{LL'} - \langle L\,|\,G\,|\,L'\rangle V_{l'})\phi_{L'} = \mu\phi_L\,,$$

which is the principle formula employed in our calculations.

The calculational procedure is therefore as follows: Determine the relevant matrix elements $\langle L|G|L'\rangle$ of the exact host Green's function. We note that one needs to know this Green's function only for values of its arguments on a single muffin-tin sphere. Determine the logarithmic derivatives for the impurity and host potentials, and solve the matrix eigenvalue equation given above. ΔZ is then given by (2.2), and $\Delta\rho$ by taking the energy derivative.

The algebraic eigenvalue equation is very easy to solve in many cases of practical interest. As is the case in the analogous Slater-Koster formalism,[24] one need only work with the sub-block of the matrix corresponding to values of L for which V_l is nonzero. If we assume that the V_l are negligible for $l > 2$, then in cubic materials the relevant matrix elements form a diagonal matrix. There are, in fact, only four independent elements, corresponding to the Γ_1, Γ_{15}, Γ_{12}, and $\Gamma_{25'}$ representations of the cubic group. One then has the very simple formula

$$\Delta Z(E) = \frac{2}{\pi}\,\mathrm{Im}\sum_L \ln(1 - \langle L|G|L\rangle V_l),$$

which can be written in a Friedel[11] form as

$$\Delta Z(E) = \frac{2}{\pi}\sum_L \tilde{\delta}_L(E); \tag{2.3}$$

the phase shifts being defined by the expressions

$$\tilde{\delta}_L(E) = \mathrm{Im}\,\ln(1 - \langle L|G|L\rangle V_l).$$

This particular model of an alloy has been considered by both Beeby[25] and Harris,[26] who also derived formulas for the change in density of states. However, their formalism is designed to yield only that part of $\Delta\rho$ associated with the volume interior to the impurity sphere, whereas ours yields the complete quantity. More formally, let $\rho(E,\vec{r})$ denote the energy and spatial density of states. Our $\Delta\rho(\epsilon)$ is the change in this quantity integrated over the entire crystal, whereas the other authors deal with the same quantity integrated over the interior of the impurity sphere. The latter procedure would be entirely inadequate in our case, since the states in question are by no means confined to the mentioned volume.

III. CALCULATION OF GREEN'S FUNCTION FOR COPPER

The bulk of the numerical work in our problem consists in the evaluation of the matrix elements of the host Green's function. The only saving feature is that for a material such as copper and the sort of impurities we envision "inserting" into copper, one need consider only the s, p, and d logarithmic derivatives. Hence there are only four matrix elements of G to be calculated.

The procedure we follow is simply to solve the basic equation

$$G = P + P\mathcal{V}G,$$

which yields the host Green's function in terms of the free-electron Green's function P and the host crystalline potential $\mathcal{V}$. One uses the Bloch theorem to simplify the problem, and also the fact that we only need to know G "on" the muffin-tin sphere. The derivation of the relevant formula is set out in detail in Ref. 23. Our starting point here will be Eqs. (48) and (49) of that paper, which show that

$$G_{LL} = \kappa j_l(j_l C_l - \eta_l) - \kappa(j_l C_l - \eta_l)^2 g_l, \tag{3.1}$$

where $\kappa = \sqrt{E}$, the Bessel functions have the argument κR, and $C_l = \cot\delta_l$, δ_l being the phase shift for each copper potential. The quantity g_L is given by

$$g_L = \frac{1}{N}\sum_k{}' \,(\tilde{C} + \tilde{B}^k)^{-1}_{LL}\ , \tag{3.2}$$

where $\tilde{C}$ is the diagonal matrix formed from the $\{C_l\}$, and $\tilde{B}^k$ is the matrix introduced by Kohn-Rostoker.[27]

The evaluation of Eq. (3.2) is the most difficult part of the calculation. g_L has both real and imaginary parts; the imaginary part arises from the poles of the matrix inverse and in fact in proportional to $\delta[\det(\tilde{C} + \tilde{B}^k)]$, while the real part is given by the Brillouin-zone integration of the principle part of the inverse. We avoid doing the three-dimensional principle-part integration by invoking the analytic properties of the Green's function: the imaginary part is determined by its explicit definition in terms of δ functions, and the real part by doing a Kramers-Kronig transformation on the imaginary.

To evaluate $\mathrm{Im}\,g_L$ we diagonalize the real symmetric matrix $\tilde{C} + \tilde{B}^k$. Let $\tilde{U}$ be the transformation matrix and $\tilde{\lambda}$ be the diagonal matrix formed from the eigenvalues; then

$$(\tilde{C} + \tilde{B}^k)^{-1}_{LL} = \sum_p |U_{L,p}|^2(\lambda_p)^{-1}.$$

Since the energy E has an infinitesimal negative imaginary part, and the eigenvalues λ_p are real for real energies, one has the relation

$$\mathrm{Im}(\lambda_p)^{-1} = \pi\,\mathrm{sgn}\left(\frac{d\lambda_p}{dE}\right)\delta(\lambda_p)$$

which leads to the expression

$$\mathrm{Im}\,g_L = \frac{\pi}{N}\sum_{n,k} |U_{L,(nk)}|^2 \delta(E - E_{nk})\left(\frac{d\lambda_{nk}}{dE}\right)^{-1},$$

where λ_{nk} is the particular eigenvalue of $(\tilde{C} + \tilde{B}^k)$ which vanishes for the energy eigenvalue E_{nk} and $U_{L,(nk)}$ is the associated eigenvector.

Introduction of the diagonal matrix $\tilde{\lambda}$ considerably reduces the numerical problems in finding the poles. A plot of the eigenvalues for some arbitrary wave vector is given in Fig. 1(b). The point to be noted is that any branch is a smooth monotonically decreasing function in the neighborhood of its zero. It is this feature which facilitates calcula-

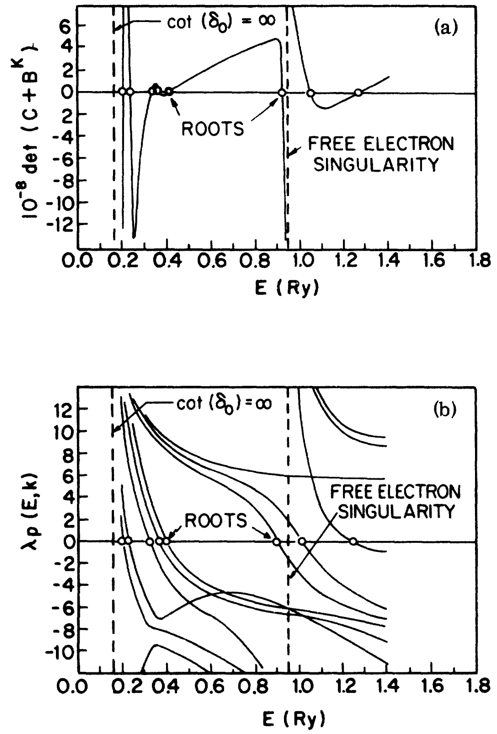


FIG. 1. Energy-dependent determinant for an arbitrary k point. The energy eigenvalues are indicated by open circles. The full determinant is displayed in (a) and the components of the diagonal form in (b). The advantages of the latter form are apparent.

tion of the weight of the δ function. This is true even if this is near a free-electron singularity.[28] In Figs. 1(a) and 1(b) we compare the behavior of $\det(\tilde{C}+\tilde{B}^k)$ as a function of energy to that of the λ's and the advantages of the latter are apparent. A point not shown on these plots is that there is also no need for special treatment of degenerate roots when the λ matrix is introduced.

The only troublesome singularities are those due to the cotangents of the phase shifts. To find $G_{L,L}$ in such a region we reformulate Eqs. (3.1) and (3.2) in terms of the tangent of the phase shifts.

For our actual calculation for copper we used the potential of Chodorow[29] and a lattice constant of 6.83097 Bohr radii. We divided the energy scale into three regions: For the lower region, 0.02–0.50 Ry, and for the upper region, 1.0–1.9 Ry, we did calculations for 89 k points within $\frac{1}{48}$ of the Brillouin zone; for the region about the Fermi energy we used a set of 505 k points in $\frac{1}{48}$ of the zone or 16 384 points in the full zone.

The λ's were evaluated on an energy mesh of 0.04 Ry and the zeros were found by a four-point polynomial fit of each λ_p about its zero. The slopes were found using the same polynomial. At the interpolated zero, λ_{nk} was evaluated to find $U_{L,(nk)}$ at this eigenvalue. This also gave an error check on the interpolated E_{nk}. This error was no larger than 0.002 Ry. Our eigenvalues for copper were in agreement with the augmented-plane-wave calculations of Burdick.[30]

Once we have E_{nk}, $d\lambda_{nk}/dE$, and $U_{L,(nk)}$ for our set of wave vectors, we can calculate the imaginary part of the Green's function and the density of states for copper using the histogram method. In Fig. 2 we compare our calculation for copper's density of states to one by Faulkner *et al.*[31] This represents a good test of our histograms and our choice of k mesh. It is apparent that we have not used a sufficient number of points to obtain the resolution of Faulkner, but still the general agreement is good.

Once we know $\mathrm{Im}G_{LL}$ we can calculate the real part using the Kramers-Kronig relation

$$\mathrm{Re}G_{LL}(E)=-\frac{1}{\pi}-\!\!\!\!\!\!\int_0^\infty \frac{\mathrm{Im}G_{LL}(\omega)}{\omega-E}\,d\omega. \qquad (3.3)$$

In practice our knowledge of $\mathrm{Im}G_{LL}$ is limited to some relatively low-energy region. We need some approximate representation of $\mathrm{Im}G_{LL}$ at high energies in order to do the integral in Eq. (3.3). To this end it is convenient to introduce Anderson's[32] representation of $G_{LL}(E)$:

$$G_{LL}(E)=\kappa(\mathcal{J}_l\mathcal{N}_l+h_L\mathcal{J}_l^2),$$

where

$$\mathcal{J}_l=\cos\delta_l j_l-\sin\delta_l n_l$$

and

$$\mathcal{N}_l=\cos\delta_l n_l+\sin\delta_l j_l.$$

The form of h_L is generally very complex for a multiple scattering problem. However, if one had only a single scatter, then $h_L=i$. We will assume that the single scatter limit is a reasonable representation of $G_{LL(E)}$ at high energies. We then have the expression

$$\mathrm{Re}G_{LL}(E)\cong-\frac{1}{\pi}-\!\!\!\!\!\!\int_0^{E_m}\left(\frac{\mathrm{Im}G_{LL}(\omega)-(\sqrt{\omega})\mathcal{J}_l^2(\omega)}{\omega-E}\right)d\omega$$
$$+(\sqrt{E})\mathcal{N}_l(E)\mathcal{J}_l(E).$$

In fact, this approximation is valid since our calculated $\mathrm{Im}G_{LL}$ is closely approximated by $(\sqrt{E})\mathcal{J}_l^2(E)$ about the neighborhood of the cutoff energy E_M.

IV. IMPURITY POTENTIAL

We now turn to the more difficult question of finding a reasonable approximation to the impurity potential within the constraints imposed by the muffin-tin model. The perturbation introduced by the impurity must vanish outside of a spherical region of radius R, and consequently can influence

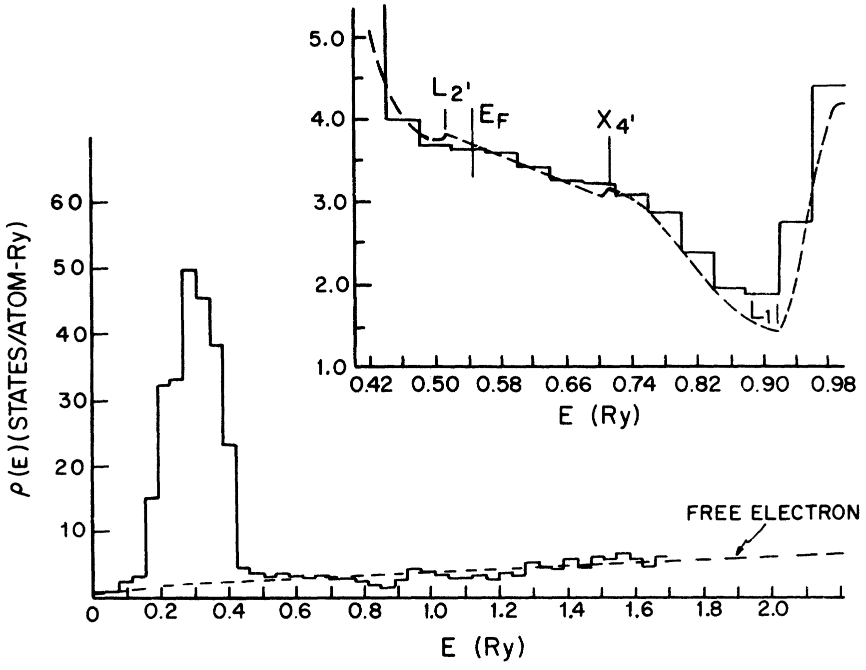


FIG. 2. Density of states for copper. The solid curve is the present work using 505 *k* points with $\frac{1}{48}$ of the Brillouin zone. In the upper curve the dotted line is from Faulkner *et al.* (Ref. 14) who used many more *k* points in the Brillouin zone.

neither the neighboring host potentials nor the constant potential between the muffin-tin spheres. In other words, to stay within the model we must assume that the perturbation introduced by the impurity is entirely screened within its own muffin-tin radius.

Meyer *et al.*[33] have shown that, because of the relatively short screening length in metals, the perturbation is roughly of the required form. They show that the impurity potential can be written as the sum of a bare potential U plus a constant term, arguing that a screening charge is drawn in around the impurity creating a spherical shell of charge about the impurity, thereby producing a constant potential term inside the shell. In this approximation the impurity potential can be expressed as

$$V = U + U_S ,$$

where U is the unscreened impurity potential in a copper environment and U_S is the above-mentioned constant. The bare potential U is constructed using the usual methods of band theory[34]; i.e., it is constructed from Herman-Skillman[35] atomic potentials using the Slater approximation where the total Coulomb potential and charge density at an impurity site is represented by atomic terms of the impurity plus the spherical terms due to copper potentials at all other lattice sites. An exchange factor of $\frac{5}{6}$ is used for all impurities potentials.

The constant term U_S can be found self-consistently using Eq. (2.3), i.e., U_S can be chosen so that at the Fermi[36] energy of the system the resulting impurity phase shifts satisfy the sum rule where ΔZ is the total change in the number of states due to an impurity.

This model for screening, along with the sum rule, also enables us to approximate the influence of local lattice displacements due to the impurity. Blatt,[37] Harrison,[38] and Ziman[39] have suggested that the effect of local lattice displacements about the impurity may be accounted for, at least in large measure, by a suitable modification in Eq. (2.3). This modification incorporates the effect of lattice distortions in an approximate way through the use of an effective valance change $\Delta Z'$, namely,

$$\Delta Z' = Z^i - Z^0(1 + \delta V/V),$$

where $\delta V/V$ is the average change of volume in a unit cell due to the impurity, and Z^i and Z^0 are the valence charges of the impurity and host, respectively.

This approximation has proved useful in rationalizing residual resistivity data in copper alloys.[37] The use of this approximation to calculate our potential stretches the bounds of this model. Recall that our formalism assumes the impurity is completely screened within a sphere of radius R, while any displacement effects extend well beyond this sphere. In order to get some estimate of the effect of displacement we will calculate the potentials using this model and compare the results with potentials that do not include displacement corrections. For $\delta V/V$ we use values given by Blatt.[37]

V. RESULTS

In Table I we list the calculated phase shifts $\delta_l(E)$, their energy derivatives $\delta_l'(E)$, and the change in density of states $\Delta\rho$ for various dilute alloys of copper at the Fermi energy E_F. The d phase shifts are defined from the representation Γ_{12} and Γ_{25}' as

$$\delta_{l=2}=\tfrac{1}{5}(2\delta_{\Gamma_{12}}+3\delta_{\Gamma_{25'}}).$$

This allows Eqs. (2.1) and (2.2) to take the form

$$\Delta\rho(E)=\sum_l \Delta\rho_l(E), \qquad (5.1)$$

where

$$\Delta\rho_l(E)=(2/\pi)(2l+1)\delta_l'(E)$$

and

$$\Delta Z=\frac{2}{\pi}\sum_l (2l+1)\delta_l(E_F). \qquad (5.2)$$

For each alloy we list two sets of numbers, one calculated using the actual ΔZ in the self-consistency requirement [Eq. (5.2)], the other using Blatt's modified values $\Delta Z'$.

In Fig. 3 we have plotted the change in density of states $\Delta\rho$ as a function of effective ΔZ. Curve (a), which passes through the origin, indicates impurities which belong to copper's row of the Periodic Table. Curve (c) shows the same for the silver row and curve (b) represents the rigid-band model.[11,12]

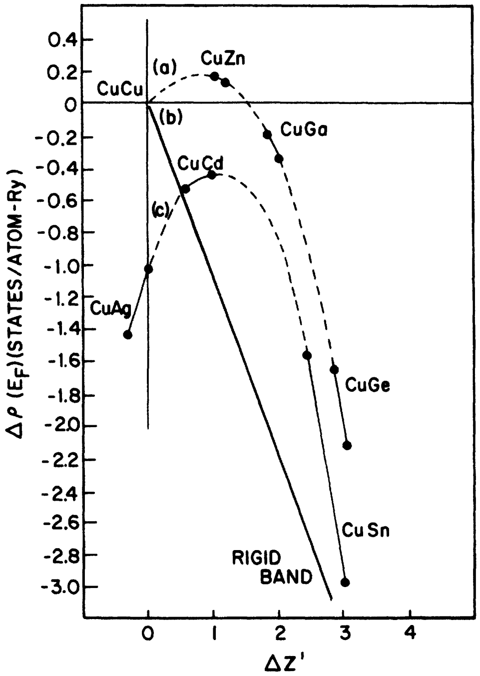


FIG. 3. Change in the density of states of copper per impurity atom. Curves (a) and (c) indicate the results for impurities from the copper and silver rows of the Periodic Table, respectively, while curve (b) displays the results of the rigid-band model. Within each material the two solid dots indicate impurity potentials with and without corrections for lattice displacement referred to in the text.

Clearly, the curves show a dependence upon the row of the Periodic Table and a dependence upon valence change within a row of the Periodic Table, The period effect shows relatively little dependence on valence difference, since the curves are approximately the same except one is shifted from the other.

The rigid-band results, curve (b), have little

TABLE I. Calculated values for the effective phase shifts $\delta(E)$ and their energy derivative $\delta'(E)$ for different dilute alloys of Cu. The Fermi energy is 0.56 Ry.

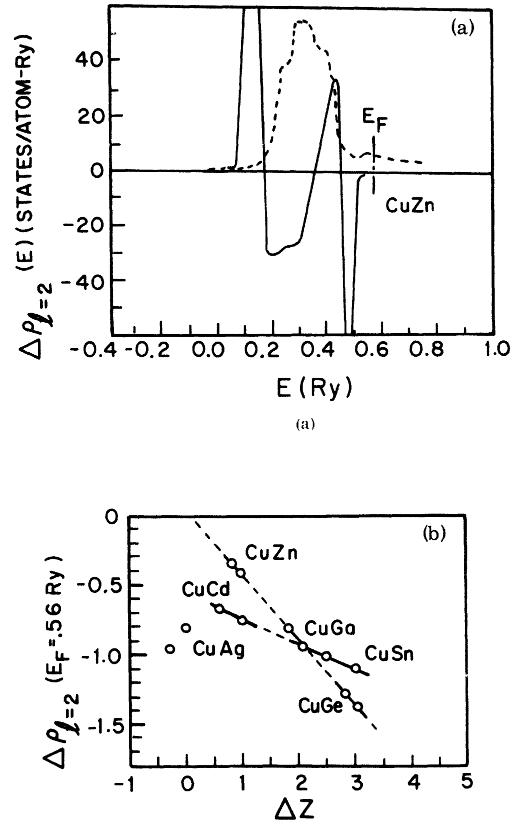
Alloy	$\Delta Z(E_F)$	$\Delta\rho(E_F)$	$\delta_0(E_F)$	$\delta_0'(E_F)$	$\delta_1(E_F)$	$\delta_1'(E_F)$	$\delta_2(E_F)$	$\delta_2'(E_F)$
CuAl	2.00	−1.02	0.53	−0.87	0.50	0.73	0.22	−0.58
	1.87	−0.87	0.50	−0.81	0.46	0.73	0.21	−0.55
CuZn	1.00	0.17	0.41	−0.68	0.28	0.53	0.07	−0.13
	0.89	0.17	0.37	−0.61	0.24	0.49	0.06	−0.12
CuGa	2.00	−0.35	0.70	−1.15	0.58	0.65	0.14	−0.27
	1.84	−0.19	0.66	−1.08	0.52	0.69	0.14	−0.25
CuGe	3.00	−2.11	0.99	−1.43	0.94	0.08	0.18	−0.42
	2.81	−1.62	0.95	−1.39	0.86	0.28	0.18	−0.40
CuAg	0.0	−1.04	0.10	−0.28	0.01	−0.03	−0.03	−0.25
	−0.32	−1.43	0.02	−0.13	−0.06	−0.21	−0.07	−0.30
CuCd	1.00	−0.42	0.38	−0.79	0.29	0.44	0.06	−0.24
	0.54	−0.54	0.24	−0.51	0.14	0.24	0.04	−0.21
CuSn	3.00	−3.00	0.85	−1.55	1.01	−0.44	0.17	−0.37
	2.42	−1.56	0.74	−1.38	0.78	0.17	0.15	−0.32
CuAu	0.0	−1.52	0.14	−0.38	0.00	−0.06	−0.03	−0.36

resemblance to our calculations. The greatest qualitative discrepancy is for Ag in Cu for which the rigid-band model shows no effect while ours shows an appreciable change.

To gain some understanding of the valence dependence within a row of the Periodic Table it is convenient to look at $\Delta\rho_2$ and $\Delta\rho_0+\Delta\rho_1$ of Eq. (5.1) separately. Let us first look at the $l=2$ component of our change in density of states, $\Delta\rho_2$. Consider a hypothetical system where the $l=0$ and $l=1$ logarithmic derivatives for the impurity are equal to those of copper. How do we expect the density of states to change? First, if we consider copper's *d* band as a simple tight-binding band whose bandwidth is a function of the number of copper atoms, then the removal of an atom results in a narrowing of the band. Replacing this vacancy with an impurity having *d* states lower in energy than those of copper introduces either a virtual state or a localized state. For an impurity state below the conduction band of copper, e.g., Sn or Ge, we have a true localized state. On the other hand, for Zn and Ag the *d* levels fall within the Cu bands giving a virtual state of a finite half-width. If this were the complete picture there would be no impurity effect at the Fermi energy. But of course it is not the complete picture, since we have not included the effect of *s-d* hybridization. In pure copper the states above the nominal *d* band have a large *d* component due to hybridization, the effect of which is to increase the density of states at E_F. When some *d* states are lowered in energy the density of states at energies above the nominal *d* position is reduced.

In Fig. 4(a) we have plotted $\Delta\rho_2$ vs E for Zn in Cu as the solid curve. The dotted curve is the density of states per atom for pure copper.[40] All of the features may be interpreted. The large positive peak is the virtual bound state associated with the *d* states of Zn. Except for Zn and Ag all other impurities for which we have done calculations have localized impurity *d* states. The general negative character in the bulk of the *d* band reflects the removal of states from the continuum formed by the *d* states of Cu, since there is in fact one less Cu atom in the alloy than in the perfect crystal. The rapidly varying region of positive and negative $\Delta\rho_2$ reflects the fact that the tight-binding type of band formed from the remaining Cu *d* states is narrower than that of pure Cu, since the hopping possibilities for a *d* electron have been reduced by the shifting down in energy of one set of atomic *d* levels. The very small negative region near E_F reflects the reduction in hydridization discussed above.

In Fig. 4(b) we plot $\Delta\rho_2$ at E_F for different impurities. We see a decrease as the *d* bands become lower in energy with increase in ΔZ. All impurities show an approximately linear behavior within their row of the Periodic Table with the exception of silver. This may indicate an error in our potential for silver. This is to be expected since band theorists have not been able to calculate a reasonable *d* band for silver from Herman-Skillman potentials without going to a self-consistent calculation.



(a)

FIG. 4. Change in the $l=2$ component of the density of states of copper per impurity atom. In (a) the solid curve is $\Delta\rho_2$ for CuZn as a function of energy, and the dotted curve is the density of states per atom for Cu. In (b) we display this component at the Fermi energy for different alloys of copper and different potentials for the same impurity.

We turn to the change in density of states produced by the difference between the impurity and host logarithmic derivative for $l=0$ and $l=1$. The general nature of the results is illustrated in Fig. 5(a), in which the dotted curve is again the density of states per atom for pure Cu, while the solid curve is $\Delta\rho_0+\Delta\rho_1$ defined in Eq. (5.1). One sees that there is a general tendency for this quantity to be negative in the center of the nominal *d*-band complex and positive near the wings. The size and sign of $\Delta\rho_0+\Delta\rho_1$ near E_F will obviously be strongly impurity dependent.

There are various effects which could be caus-

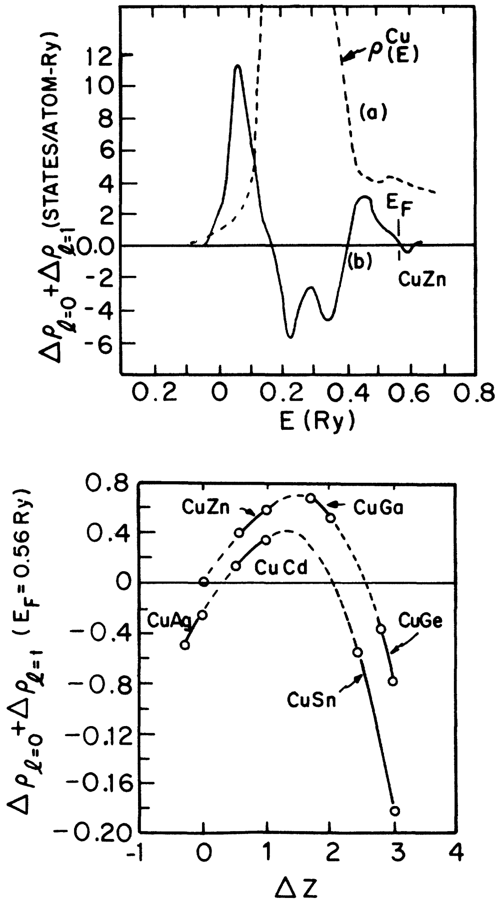


FIG. 5. Change in $l=0$ and $l=1$ components of the density of states of copper per impurity atom. In (a) the solid curve is $\Delta\rho_0+\Delta\rho_1$ for CuZn as a function of energy, and the dotted curve is the total density of states for Cu. In (b) we display this component at the Fermi energy for different alloys of copper and different potentials for the same impurity.

ing the shape of $\Delta\rho_0+\Delta\rho_1$ in the d-band region, all of which are inextricably mixed. For example, in the language of the combined interpolation scheme,[41] the general effect of alloying on the plane waves (mostly s and p) would be to lower the energy of these states. If we hypothetically fix the $l=2$ logarithmic derivative we are effectively constructing an alloy in which the tight-binding states are unchanged, but for which the plane-wave continuum is lower in energy than it is for the perfect host. This will tend to have the effect of making a somewhat broader tight-binding–plane-wave d-band complex. Furthermore, the nominal d tails of pure Cu contain a significant s-p component. Impurity scattering through these parts of the d-band wave function will tend to broaden the peak in the unperturbed density of states.

In our particular region of interest, near the Fermi energy, the behavior is not rigid-band-like. In Fig. 5(b) we have plotted $\Delta\rho_0+\Delta\rho_1$ at E_F for different impurities. For small ΔZ we have a positive value for $\Delta\rho_0+\Delta\rho_1$ which becomes negative as ΔZ becomes large. This does not reflect any simple model behavior but presumably reflects the detailed nature of the energy bands of copper and how they interact with an impurity.

VI. COMPARISON WITH SPECIFIC-HEAT DATA

The motivation for our calculation was the existence of unexplained specific-heat data for several dilute copper (and other noble-metal-based) alloys, the feature of particular interest being the increase of the coefficient of the linear term upon the addition of pentavalent elements.

The quantity of interest is

$$\left(\frac{d\ln\gamma}{dc}\right)_{c\to 0},$$

where the $c\to 0$ limit reflects the fact that the data refer to the extreme dilute limit. The total concentration derivative may be divided into two parts:

$$\left(\frac{d\ln\gamma}{dc}\right)_{c\to 0}=\left(\frac{\partial\ln\gamma}{\partial c}\right)_{V}+\left(\frac{\partial\ln\gamma}{\partial\ln V}\right)_{c=0}\frac{d\ln V}{dc}\ . \qquad (6.1)$$

The second term refers to the mean volume change produced by adding impurities to the system. The factor $\partial\ln\gamma/\partial\ln V$ is evaluated at $c=0$, and is therefore a property of the perfect host. This derivative, the low-temperature electronic Grüneisen constant, has been measured for Cu by Carr *et al.*[42] and found to have the value 0.63 ± 0.06, essentially the same as the free-electron value 0.67. The factors $\partial\ln V/\partial c$ have been measured for a variety of alloys.[37] Consequently, the second term can

TABLE II. Comparison of the calculated change in density of states with the measured change in the coefficient of the linear term in the low-temperature specific heat. The measured values $\partial\ln\gamma/\partial c$ have been corrected for volume changes as described in the text. V_1 and V_2 are, respectively, the theoretical values for $\partial\ln\rho/\partial c$ for the present work with and without corrections for the lattice displacements referred to in the text; the last column is the rigid-band results for the theoretical value of $\partial\ln\rho/\partial c$ for comparison.

Alloy	Experimental Volume corrected	Theory V_1	 V_2	 Rigid-band
CuZn	0.13[a], 0.16[b], 0.25[c]	0.045	0.046	−0.301
CuGa	0.56[a]	−0.052	−0.097	−0.602
CuGe	0.69[a]	−0.448	−0.584	−0.903
CuAg	−0.35[d]	−0.392	−0.290	0.0
CuSn	0.35[b]	−0.430	−0.828	−0.903

[a] Reference 10.
[b] Reference 7.
[c] Reference 2.
[d] Reference 6.

be computed, and subtracted from the experimentally measured total derivative.

The first term in the decomposition (6.1) is the fractional rate of change in γ that would occur if the volume per atom of the alloy were the same as that of the undisturbed host. In the simplest model—the independent-particle picture in which electron-phonon and residual electron-electron interactions are neglected—the coefficient γ is directly proportional to the density of electronic states at the Fermi energy. Its derivative, therefore, would in this model be given by the expression

$$\frac{d\ln\gamma}{dc} = \frac{1}{\rho_0}\Delta\rho ,$$

where ρ_0 is the Fermi-level density of states per atom in the host.

However, a considerable discrepancy still exists (see Table II). In spite of the fact that we have made some simplifying assumptions in constructing a tractable model of the alloy, the model is sufficiently detailed that it seems unlikely that further refinement of an independent-particle model will bring theory very much closer to experiment. One must then look for other mechanisms, the most likely of which is the change in the electron-phonon enhancement factor upon the addition of the impurities to copper.

ACKNOWLEDGMENTS

The authors wish to express appreciation to Dr. Harold Davis of Oak Ridge National Laboratory for an efficient program for calculation of KKR structure constants, and to Professor Sohrab Rabii of the Moore School of Electrical Engineering of the University of Pennsylvania for a program for calculation of crystal potentials.

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[*] Supported in part by the National Science Foundation and the Advanced Research Projects Agency.

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