Auger line shape in alloys

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(Received 14 July 1983)

A theory for Auger line shapes in alloys is presented and applied to dilute alloys with "free-electron"-like and "noble-metal"-like hosts. For noble-metal-like hosts, we show that anomalous impurity Auger line shapes can be expected. The theory is developed for degenerate d states, for which we determine the conditions under which the atomic-split two-hole terms can be treated independently. The Auger line shape for more concentrated alloys is discussed qualitatively and is shown to yield information about the nearest-neighbor surroundings.

I. INTRODUCTION

Several years ago it was pointed out that Auger spectroscopy can provide direct evidence for the importance of electron correlation effects in transition metals.[1−3] In those papers and subsequent reviews[4−6] it has been shown that a comparison of the Auger spectrum with the self-convolution of the one-particle density of states yields a measure of the hole-hole Coulomb interaction. It has also been shown that as electron correlation effects become increasingly important the Auger spectrum will evolve into a quasiatomiclike spectrum from a broad-band-like spectrum as would be obtained for negligible correlations.[7] The shape as well as the position of the Auger lines provide valuable information concerning the importance of electron correlation effects.

The theories mentioned above are applicable to pure metals for which the valence-band structure is approximated by a single band which is assumed to be initially full. Approximate theories for partially filled bands have also recently been developed.[8,9] Numerous experimental results have recently been reported on alloys and intermetallic compounds[10−13] in which a straightforward application of the Cini-Sawatzky theory has been shown to yield anomalous results not at all in agreement with experiment. The main problem as pointed out recently[10] is that there are several bands of importance in the valence-band region which can lead to strong broadening effects in the Auger spectra. In this paper we develop a theory for the Auger spectra of alloys taking into account the multiple band structure, but still with the assumption that all relevant bands are initially full. We show that Auger spectra in these materials can be strongly distorted by the presence of other bands and that the spectral shape provides information about the interband mixing due to hybridization.

The theory is first developed for dilute impurity systems and then extended to intermetallic compounds. For the impurity system we describe first a general theory for the Auger line shape for orbitally nondegenerate bands and then apply it to two kinds of impurity systems, namely an impurity in an sp free-electron-like host and an impurity in a noble-metal-like host. The Auger line shape for these two systems differs strongly and provides infor-

mation on the impurity Coulomb interactions as well as the impurity-host hybridization. To illustrate the physics the experimental Cu Auger spectra of Cu-Cd alloys are presented and discussed. We then develop a general theory for treating the nondegenerate d impurity Auger spectra with strong atomic term splittings and show that in many cases the atomic terms can be treated independently. Finally we discuss qualitatively the Auger spectra of more concentrated alloys and show that the Auger line shape can provide information about the local surroundings of the Auger emitting atom.

II. GENERAL IMPURITY THEORY

For the general theory we consider a Hamiltonian of the form

$$H = H_1 + U d_{0\uparrow} d_{0\uparrow}^\dagger d_{0\downarrow} d_{0\downarrow}^\dagger . \tag{1}$$

Here H_1 is a one-electron Hamiltonian describing the host band structure and the impurity-host hybridization as well as the one-electron part of the impurity. The second term describes the Coulomb interaction of two holes on the impurity. Although we will be interested in transition-metal impurities, we have, in the above, neglected the d-orbital degeneracy. Inclusion of the degeneracy will be discussed in Sec. VI. We have also neglected all host-host and impurity-host Coulomb interactions. We justify this as follows: To describe the impurity Auger spectrum we will want to determine the time development of a state with two holes created at time zero on the impurity, the Fourier transform of which yields the Auger spectrum. The probability amplitude that these holes will land upon the same host atom, where again the Coulomb interaction may be large, will be small, and therefore these states can be neglected. In fact the worst possible case would be that of the pure metal in which case the two-hole states on neighboring atoms are degenerate with those on central atoms. In the Cini approximation[1] to the Auger line shape for the pure metal, the Coulomb interaction is also neglected for two-hole states on atoms other than the one on which the two holes are initially created. By a comparison with the exact expression in this case,[3] we have previously shown that Cini's is in fact a good approximation,

making only small errors in the linewidth. For the alloys discussed here we expect this approximation to be even better.

The Auger line shape is given by the impurity two-hole spectral function

$$I(\epsilon) = \text{Im} \left[\frac{1}{\pi} \left\langle \psi \left| d_{0\uparrow}^\dagger d_{0\downarrow}^\dagger \frac{1}{\epsilon - H} d_{0\uparrow} d_{0\downarrow} \right| \psi \right\rangle \right] . \quad (2)$$

We consider the case where ψ (the initial ground-state wave function) contains no holes of importance to the Auger spectrum. This, for example, will be the case if the impurity state is well below the Fermi level. With the use of the relation $G = g + g H_2 G$ for the two-hole Green's function, with $H_2 = U d_{0\uparrow} d_{0\uparrow}^\dagger d_{0\downarrow} d_{0\downarrow}^\dagger$ we obtain

$$G_{00}^{00} = g_{00}^{00} + g_{00}^{00} U G_{00}^{00} , \quad (3)$$

where

$$g_{00}^{00} = \left\langle \psi \left| d_{0\uparrow}^\dagger d_{0\downarrow}^\dagger \frac{1}{\epsilon - H_1} d_{0\downarrow} d_{0\uparrow} \right| \psi \right\rangle . $$

It should be noted that g is not diagonal in this representation, but since H_2 is, only the diagonal components enter in the relation for G_{00}^{00}. The solution is then

$$G_{00}^{00} = \frac{g_{00}^{00}}{1 - U g_{00}^{00}} . \quad (4)$$

Since H_1 contains only one-electron terms

$$g_{00}^{00}(\epsilon) = (2\pi i)^{-1} \int g_0^0(\epsilon') g_0^0(\epsilon' - \epsilon) d\epsilon' ,$$

we end up with the same solution as Cini.

The Auger spectrum is given by

$$I(\epsilon) = \text{Im} \left[\frac{1}{\pi} G_{00}^{00} \right] = \frac{D(\epsilon)}{[1 - UF(\epsilon)]^2 + D^2(\epsilon)} , \quad (5)$$

where $D(\epsilon)$ is the self-convolution of the one-particle *impurity* partial density of states and $F(\epsilon)$ is given by

$$F(\epsilon) = \text{P} \int_{-\infty}^{\infty} \frac{D(\omega)}{\omega - \epsilon} d\omega .$$

The important quantity then is the complete impurity one-hole Green's function. The above solution was derived previously by Drchal and Kudrnovsky for a Clogston-Wolff[14] impurity and we repeated it here to emphasize that it is a general solution for any Hamiltonian in which the impurity-host mixing and host band structure is determined by one-electron (-hole) terms.

Although this solution is essentially the same as that given by Cini for the pure metal one must apply it with caution in alloys and compounds. The reason is that the most important part for the Auger spectrum of the one-hole impurity Green's function lies in the energy region shifted by U from the peak in the one-hole impurity density of states. For the cases where U is quite large the most important part of $g_0^0(\epsilon)$ for the Auger spectrum occurs so far removed from the peak in the impurity density of states that it cannot be determined in sufficient detail from valence-band x-ray-photoemission (XPS) or ultraviolet-photoemission (UPS) measurements. This, in

particular, is a problem if the host metal happens to have a large density of states in that energy region and the XPS or UPS spectra cannot distinguish the small impurity contribution in this region from that of the host.

III. AN EXAMPLE

To illustrate the importance of the detailed knowledge of the impurity Green's functions for energies far removed from the peaks in the impurity density of states, and to discuss the physics involved, we studied the alloys Cd_3Cu, $CdCu_2$, and Cu, concentrating on the Cu Auger spectrum. The reasons for choosing this alloy system are the following.

(1) The Cu Auger spectrum is well understood, being quasiatomiclike in pure Cu.[15,16]

(2) The Cd $4d$ band has a high density of states which happens to lie in an energy region well separated from the Cu $3d$ band but in the region where the Cu two-hole state is expected.

The valence-band spectra are shown in Fig. 1. We see that the Cu $3d$ band is considerably narrowed in the alloys as expected from a simple dilution argument. The Cd $4d$ and Cu $3d$ bands are well separated so we expect so little mixing between these bands that it would be undetectable in the one-hole spectra. If we also neglected the mixing for the self-convolution occurring in the Auger line shape, the Cu Auger spectra would be expected to be narrowed in the alloys as compared to Cu, because the linewidth for a single-band case and for large U is proportional to W^2/U^2 where W is the Cu bandwidth.

In Fig. 2 the Cu $L_3 M_{45} M_{45}$ Auger spectra are shown and some of the data is given in Table I. The Auger spectra of the alloys look very similar to those of pure copper and can be interpreted in the same way.[15,16] The structure in the shoulder at low kinetic energy is due to Coster-Kronig—preceeded Auger transitions[16] and will not further be considered here. The main peak arises from a $3d^8 \, {}^1G$ term and the smaller peak at higher kinetic energy from a ${}^3F$ term. We notice that in the alloy the ${}^1G$ region is broadened relative to pure Cu and the ${}^3F$ region is, if anything, narrowed. In terms of Eq. (4) this broadening is due to a small amount of mixing of the Cu $3d$ and Cd $4d$ bands.

To understand the physics of this we consider a different approach to the Auger-line-shape problem. The Auger line shape can also be written as

$$I(\epsilon) = \sum_n |\langle \psi_n | d_{0\uparrow} d_{0\downarrow} | \psi \rangle|^2 \delta(\epsilon - \epsilon_n) , \quad (6)$$

where ψ_n are the two-hole eigenstates with energies ϵ_n, and ψ is the initial ground state. This result is easily obtained from Eq. (2) by writing $d_{0\uparrow} d_{0\downarrow} = \sum_n \alpha_n \psi_n$ with $\alpha_n = \langle \psi_n | d_{0\uparrow} d_{0\downarrow} | \psi \rangle$. We then must obtain the two-hole eigenstates ψ_n. We consider as a basis set the following states: Two holes on $Cu \rightarrow Cu(d^8)$ with diagonal energies $2\epsilon_d^{Cu} + U$, one hole on Cu and one on $Cd \rightarrow Cu(d^9)Cd(d^9)$ with diagonal energies $\epsilon_d^{Cd} + \epsilon_d^{Cu}$, and two holes on the $Cd \rightarrow Cd(d^9)Cd(d^9)$ with diagonal energy $2\epsilon_d^{Cd}$. Since we are interested in the influence of the Cd $4d$ band on the Cu Auger spectrum we neglect for now the sp band and

TABLE I. Some relevant energies and parameters used to calculate the Auger spectra of Cu-Cd alloys. $U(^1S)=11.5$ eV, $U(^1G)=6.7$ eV, and $U(^3P)=5.8$ eV. $U(^1D)=5.6$ eV and $U(^3F)=3.7$ eV. (BE denotes binding energy.)

	Cu	Cu_2Cd	Cd_3Cu
BE Cu $2p^{3/2}$	932.2 ± 0.2	932.4 ± 0.2	932.5 ± 0.2
BE Cu $3d$	3.3 ± 0.2	3.5 ± 0.2	3.7 ± 0.2
BE Cu $4d$		10.7	10.7
Width Cd $4d$		≈1.8[a]	~2.0[a]
$E_{kin}(^1G)$	918.8	918.9	918.4
$\Delta E(^1G\text{-}^3F)$	2.7	2.75	2.9

[a]Full width at half-height.

consider Cu as a dilute impurity so that $Cu(d^9)Cu(d^9)$ states also do not contribute. We see from the energies that if $2\epsilon_d^{Cu}+U\simeq\epsilon_d^{Cu}+\epsilon_d^{Cd}$, the $Cu(d^8)$ states fall inside a continuum of states which is just the Cd $4d$ density of states shifted in energy by ϵ_d^{Cu}. This condition can also be written as

$$\epsilon_d^{Cu}+U=\epsilon_d^{Cd} . \tag{7}$$

If this is the case, the $Cu(d^8)$ state will be "lifetime" broadened. The Cd-Cu alloys were chosen because as in-

dicated in Fig. 1, the $Cu(d^8)^1G$ state fulfills the above condition, it will therefore be broadened while the ^3F state falls just outside the Cd band and should remain narrow. This is exactly what is observed in the spectra of Fig. 2. From the above argument an approximate Auger line shape for this case can easily be obtained since we are dealing with a state $Cu(d^8)$, interacting with a continuum, $Cu(d^9)Cd(d^9)$. The Auger line shape neglecting the much-higher-energy $Cd(d^9)Cd(d^9)$ states will then be given by

$$I(\epsilon)\simeq\frac{1}{\pi}\mathrm{Im}\frac{1}{\omega-2\epsilon_d^{Cu}-U-2V^2\sum_k(1/\omega-\epsilon_d^{Cu}-\epsilon_{dk}^{Cd})} , \tag{8}$$
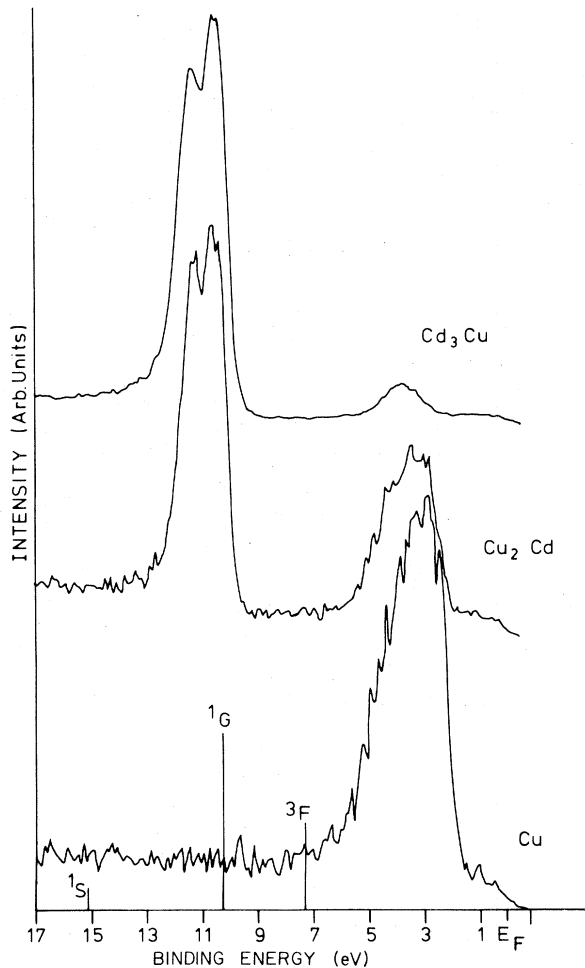

FIG. 1. Valence-band spectra of Cu, Cu_2Cd, and Cd_3Cu obtained using monochromatized Al $K\alpha$ radiation. Indicated are the relative energies of the ^3F, ^1G, and ^1S two-hole states, $\epsilon_d^{Cu}+U$.
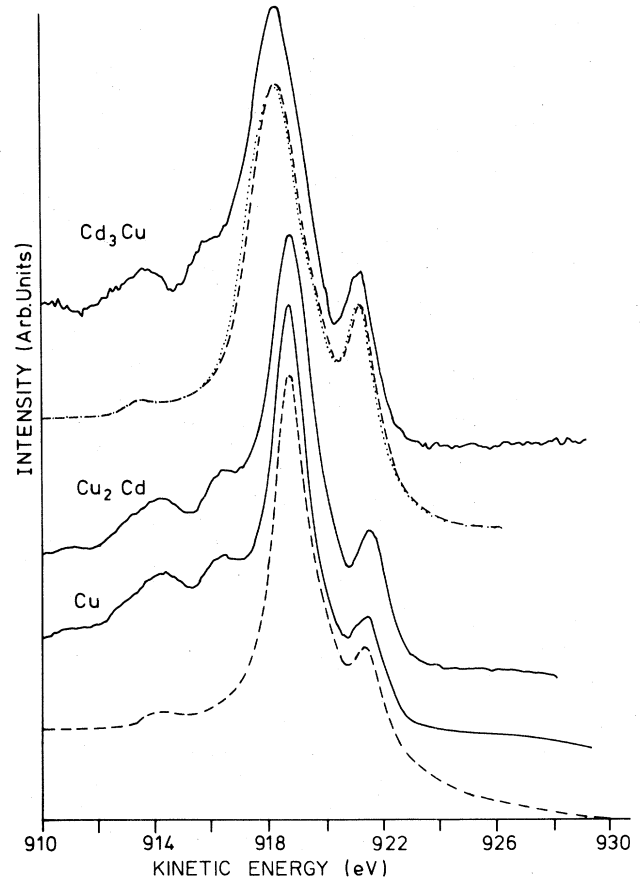

FIG. 2. Auger spectra $(L_{23}M_{45}M_{45})$ of Cu, $CuCd_2$, and Cd_3Cu. Solid lines are experimental and dashed and dotted lines are obtained as explained in the text.

where V is assumed to be k independent and is the one-particle Cd(d) Cu(d) mixing matrix element, i.e., $V = \langle \psi_{Cu} | H | \psi_{Cd_k} \rangle$ and $\epsilon = \omega + \epsilon_{2p}^{Cu}$ is the Auger kinetic energy. The factor of 2 multiplying V^2 arises because we are dealing with two-hole states, so that each hole can decay into the Cd band. This result, although approximate, gives a good description of the Cu Auger spectrum in Cu-Cd alloys. It describes the broadening of a state falling inside the continuum, such as the Cu (d^8) ^1G state, whereas states falling outside the continuum, such as the Cu$(3d^8)^3F$ state, suffer only a small shift in energy.

The dashed and dotted lines in Fig. 2 are theoretical curves obtained as follows. The d^8 final-state terms are treated independently each with a Coulomb interaction given in terms of the Slater integrals F^0, F^2, and F^4 according to relations given by Slater.[17] The F^2 and F^4 integrals were taken from recent Auger-photoelectron coincidence data of Haak[18] ($F^2 = 11.4$ eV and $F^4 = 8.7$ eV). The intensities of each term is calculated using radial integrals as given by McGuire.[19] The contributions for the various terms are then added (as justified in Sec. V) and convoluted with a 1.2-eV full width at half maximum Lorentzian to account for the core-hole lifetime, instrumental broadening, and additional broadening of the two-hole final state not accounted for by the theory.

For the pure-Cu spectrum the Cini approximation as given by Eq. (5) was used. Aside from the Coster-Kronig—preceeded Auger structure on the low-kinetic-energy side we see that the experimental spectrum is nicely reproduced by theory.

The Cd$_3$Cu spectrum was calculated in two ways. The dashed curved is obtained using the general expression, Eq. (4), and taking for the one-particle Green's function the result obtained for an Anderson impurity Hamiltonian as discussed in Sec. IV. The Cu $3d$—Cd $4d$ one-particle hybridization interaction $[\pi V^2 \rho(\epsilon)]_{av} = 0.19$ eV was a fitting parameter. The Cd $4d$ band was simulated by a semicircular density of states normalized to unit area with a width of 2 eV. The dotted curve in Fig. 2 was obtained using the same parameters but now using the approximate expression for the Auger line shape as given by Eq. (8). In this case the approximate result is almost indistinguishable from the result obtained using the more exact expression.

As observed experimentally the ^1G portion of the Cu Auger spectrum of Cd$_3$Cu is also theoretically found to be broadened relative to pure Cu. This occurs because $\epsilon_d^{Cu} + U(^1G) = 10.4$ eV falls energetically inside the Cd $4d$ band. The ^3F state on the other hand remains narrow because $\epsilon_d^{Cu} + U(^3F) = 7.4$ eV does not fall inside the Cd $4d$ band. The ^3F state does, however, suffer a small shift to higher kinetic energies because of the interaction with the Cd $4d$ band, thereby increasing the apparent ^1G-^3F splitting in Cd$_3$Cu relative to pure Cu. In pure Cu the ^3F state is shifted slightly in the opposite direction because of interaction with the Cu d band. This effect is seen from the ^1G-^3F splitting given in Table I.

The Cu$_2$Cd spectrum displays, as far as the above-mentioned effects are concerned, an intermediate case. From the broadening of the ^1G part relative to Cu we find that $[\pi V^2 \rho(\epsilon)]_{av}$ for Cu$_2$Cd is about 0.05 eV. Comparing

this to Cd$_3$Cu we see that the broadening of the ^1G is roughly proportional to the Cd concentration. Actually we expect $[\pi V^2 \rho(\epsilon)]_{av}$ to be proportional to the number of Cd nearest neighbors, as will be discussed in Sec. VII.

IV. ANDERSON IMPURITY

Up to this point we have developed a general equation describing the Auger line shape for impurity systems and have used intuitive physical arguments for an approximate simple relation to describe the Cu-Cd alloy experiments. The problem remaining is to obtain good approximations to the one-particle Green's function appearing in Eq. (4) and to justify the approximate relation suggested for alloy systems such as Cu-Cd.

There are basically two simplified Hamiltonians that are used to describe impurity systems, namely the Anderson[20] and Clogston-Wolff[21,22] Hamiltonians. Use of the Anderson Hamiltonian has been successful in describing transition-metal impurities in free-electron-like hosts such as Al, Mg, etc. The Clogston-Wolff Hamiltonian is very appropriate for describing the impurity d—host d mixing for impurities in noble metals such as Cu, Ag, and Au, as we will discuss below.

We start with the Anderson Hamiltonian for which we need to consider only the one-particle part for g_0^0 as discussed above,

$$H_1 = \sum_{k,\sigma} \epsilon_k C_{k\sigma}^\dagger C_{k\sigma} + \epsilon_d \sum_\sigma d_\sigma^\dagger d_\sigma + \sum_{k,\sigma} V_k (C_{k\sigma}^\dagger d_\sigma + d_\sigma^\dagger C_{k\sigma}) \ .$$

(9)

The impurity Green's function has been extensively discussed[23] and has the solution

$$g_0^0(\epsilon) = \cfrac{1}{\epsilon - \epsilon_d - \sum_k |V_k|^2/(\omega - \epsilon_k)} \ .$$

(10)

We first consider the case of a constant sp-band density of states and constant $V = V_k$, which is an approximation often used to describe the impurity local density of states. We show below that this is usually *not* a good approximation to describe the Auger spectrum except if U is very small compared to $\pi V^2 \rho$ where ρ is the density of states, although it is satisfactory in most cases to describe the XPS or UPS valence-band spectra. We then obtain

$$g_0^0(\epsilon) = \frac{1}{\epsilon - \epsilon_d - \pi i V^2 \rho} \ ,$$

(11)

which is just a Lorentzian often referred to as a virtual bound state. The self-convolution is then

$$g_{00}^{00}(\epsilon) = \frac{1}{\epsilon - 2\epsilon_d - 2\pi i V^2 \rho}$$

(12)

and

$$G_{00}^{00}(\epsilon) = \frac{1}{\epsilon - 2\epsilon_d - U - 2i\Gamma} \quad (\Gamma = [\pi V^2 \rho]_{av}) \ ,$$

(13)

which is just a Lorentzian with a width of 2 times that of the local one-particle density of states. The fact that this

looks much like the intuitive relation used for the Cu-Cd alloys is purely accidental, because in the Cu-Cd alloys the *one*-particle local Cu density of states is determined by a mixing with an *sp* band while the *two*-particle spectrum is determined by Cu(*d*)-Cd(4*d*) mixing.

The above relation is only valid if indeed the host-metal density of states and V_k are constant over an *energy range large compared to U*. This is seldom expected to be the case.

In cases where U is large so that the local two-hole state falls in a region of lower density of states, the linewidth of the Auger line will be less than twice that of the virtual bound state. In fact the two-hole state may even fall outside of a continuum in which case it will be a δ-function-like peak. This will occur for $2\epsilon_d + U > 2V_{int}$ where V_{int} is the internal potential describing the zero of the free-electron-like band. However, even if $2\epsilon_d + U > V_{int} + \epsilon_d$, the Auger line will already be very narrow—as we will see in the following example.

We have calculated the impurity Auger spectrum for a model free-electron-like density of states as shown in Fig. 3, with an impurity-host interaction described by the Anderson Hamiltonian. The dashed line in Fig. 3 is the local *one*-hole impurity density of states for $[\pi V_k^2 \rho(\epsilon)]_{av} = 0.4$ eV, $\epsilon_d = 3.0$ eV below ϵ_F, and $V_{int} = 8.0$ eV. The free-electron density of states integrated to the cutoff was normalized to 1.

In Fig. 4 (solid lines) we show the Auger spectra calculated for $U = 0-10$ eV, showing the change in linewidth as the two-hole state moves along to a lower density of host states. These lines are all only slightly distorted Lorentzians (a distortion which probably would not be observed experimentally) until the local two-hole state falls outside any continuum, in which case it becomes a very narrow bound state with some intensity left in the continuum region. In Fig. 5 we show a plot of the linewidth as
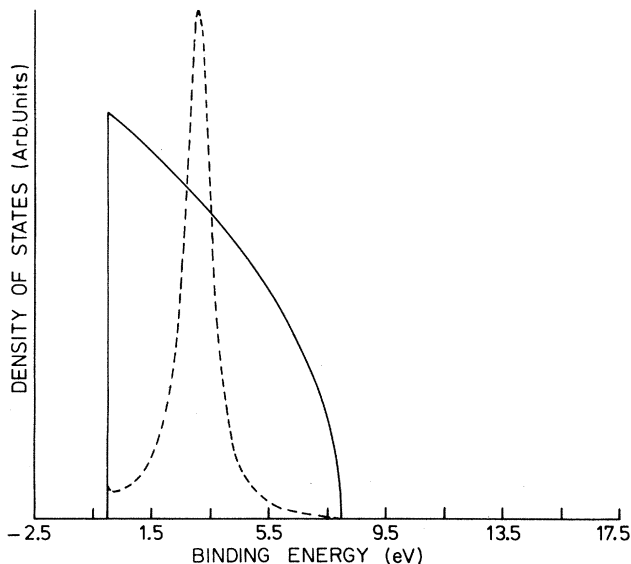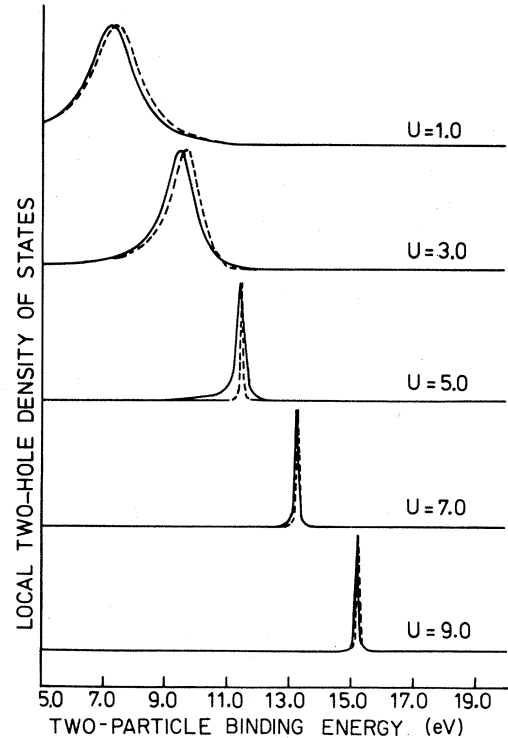

FIG. 4. Auger line shape calculated for various values of U. Solid lines plotted using Eqs. (4) and (10) and dashed lines plotted using Eq. (14) in the text.

a function of U for this model calculation (pluses). As expected we see the linewidth decrease as the two-hole state moves to a lower-density-of-states region in the host band. Even if U is so large that $\epsilon_d + U$ falls outside of the host *sp* band, i.e., $\epsilon_d + U > 8$ eV or $2\epsilon_d + U > 11$ eV (in Fig. 4

FIG. 3. Free-electron-like host (solid line) and impurity (dashed line) densities of states used in a model calculation.
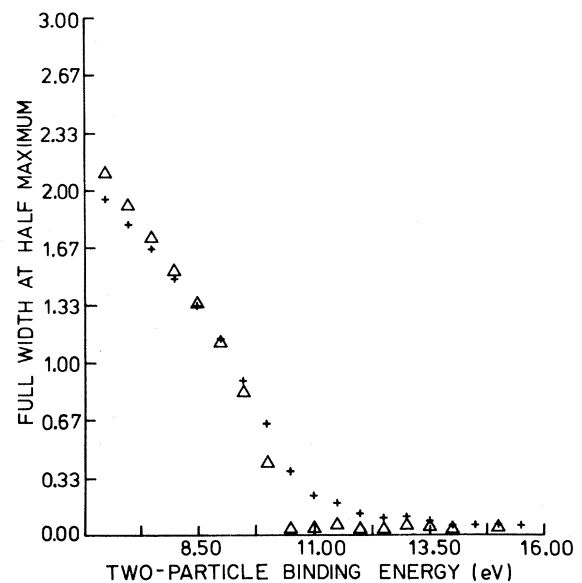

FIG. 5. Auger linewidth as a function of U for an Anderson-type impurity. Open triangles are plotted using the approximate expression [Eq. (14)] and pluses are plotted using Eqs. (4) and (10).

this corresponds to $U > 5$), the Auger spectrum still retains some width. This is because the local two-hole state still falls in a continuum resulting from the self-convolution of the free-electron density of states. In this case both holes can simultaneously move into the sp band.

Aside from this small broadening for large U values these spectra can in fact be well described by a simple relation as used for the Cu-Cd alloys. This expersion derived in the Appendix is of the form

$$G_{00}^{00}(\epsilon) = \frac{1}{\epsilon - 2\epsilon_d - U - 2 \sum_k (V_k)^2/(\omega - \epsilon_k - \epsilon_d)} . \quad (14)$$

The dotted lines in Fig. 4 and open triangles in Fig. 5 are the results of using this simple expression. We see that the only significant differences occur if $\epsilon_d + U > V_{int}$, for which the approximate expression gives a bound state, whereas the exact line shape has a small width. This can be understood because in the approximate expression we have not included the possibility that both holes move simultaneously from the impurity state to the continuum, which now involves the self-convolution of the free-electron-like band. The broadening due to this process will be small because the convoluted density of states is lower and can be described as a second-order process.

V. CLOGSTON-WOLFF HAMILTONIAN

More interesting than the free-electron-like hosts are the noble-metal hosts. The high density of d states in these hosts can lead to very strong non-Lorentzian-broadening of the impurity Auger lines especially if $\epsilon_d + U$ falls in the host d-band region. These Auger spectra can again be described by Eq. (1), but just as in the free-electron-like hosts we require information about $g_0^0(\epsilon)$ far away (U) from the impurity one-hole peak in the density of states. In systems such as Pt, Pd, and Ni impurities in Cu, Ag, and Au the impurity local d density of states exhibits one or more peaks between the Fermi level and the host d band.[24,25]

The local impurity partial density of states in the host d region is difficult to obtain accurately from XPS or UPS data because of the large contribution from the host d band.[24] The d-d mixing, however, can be quite accurately described by a Clogston-Wolff[21,22] Hamiltonian, especially for CuNi, AgPd, and AuPt, since here the d wave functions of host and impurity have almost the same radial extent. The Clogston-Wolff Hamiltonian reads

$$H = \sum_k \epsilon_{d_k} C_{d_k} C_{d_k} + \Delta C_{d_0}^\dagger C_{d_0} , \quad (15)$$

where $C_{d_k}^\dagger$ are creation operators for the host d band and the last term describes a shift of the d-electron energy if it is on the impurity site (site 0). The one-particle impurity Green's function is then given by

$$g_0^0 = \frac{\Gamma_0^0}{1 - \Delta \Gamma_0^0} , \quad (16)$$

where Γ_0^0 is the local host Green's function in the absence of the impurity. We have

$$\Gamma_0^0 = \sum_k \frac{1}{\omega - \epsilon_{d_k}} . \quad (17)$$

The details of Γ_0^0 are determined by the host-metal d-band structure. In the Auger-line-shape equation we require the self-convolution of g_0^0, which in general must be determined numerically. To show what happens to the Auger line shape we considered the host d band to be semicircular and calculated the Auger line shape for various values of U, taking Δ so that the impurity one-hole d state lies between the semicircular host band and the Fermi level. For the calculation the host bandwidth is taken to be 3 eV starting at 3.5 eV below ϵ_F, which is characteristic of Ag. To show only the influence of the host d band we have neglected the sp-band mixing resulting in a δ-function peak for the impurity state outside of the host d band. The influence of the sp band will be discussed below. In Fig. 6 we show the host-model density of states as used (solid line) and the impurity partial density of states (dashed line) displaying the sharp bound state and the impurity partial density of states in the host d band. In Fig. 7 we show the resulting Auger spectra. Here we see that as soon as $\Delta + U$ is such that the two-hole state falls inside the host d band, it is strongly broadened and then narrows again as soon as $\Delta + U$ is outside the host d band.

The strong variation of the Auger line shape with U can result in rather anomalous line shapes for d impurities. Because of the d degeneracy the final two-hole states are strongly split into terms because of the d-d Coulomb integrals F^2 and F^4. For a d^8 configuration in LS coupling we have the states ^1S, ^1G, ^3P, ^1D, ^3F with energy splittings of the order of 5—8 eV for Ni and Pd. Treating each of the terms separately with the above theory results in.a dif-
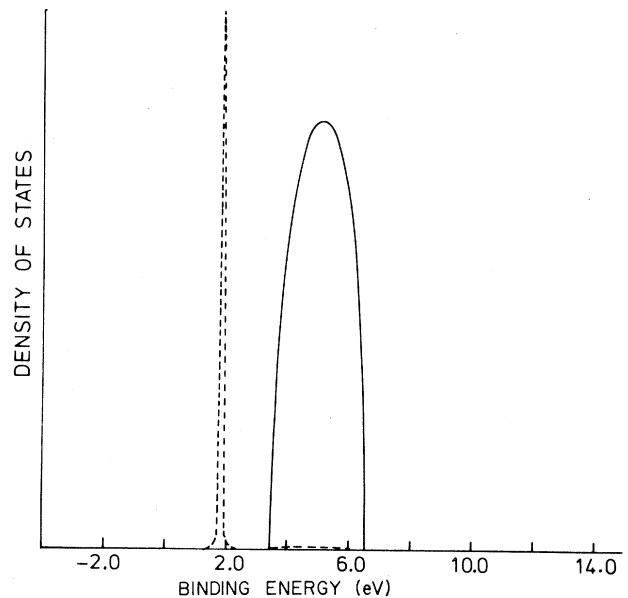

FIG. 6. Model host (solid line) and impurity partial (dashed line) densities of states used for the Clogston-Wolff calculation. The impurity energy was taken at 2 eV.
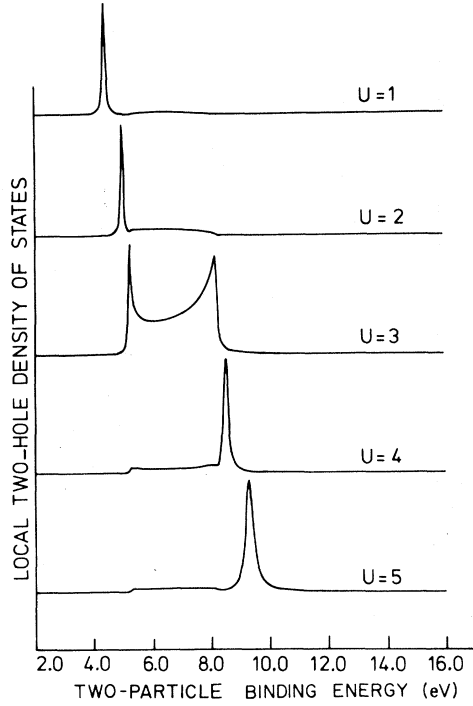
FIG. 7. Auger spectra calculated for the impurity density of states shown in Fig. 6 as a function of the correlation energy U.

ferent U_{eff} for each term so that some terms can fall inside the host d band and others outside the host d band. This is the case for Pd in Ag leading to the anomalous line shape.[11] In a subsequent paper we show that the Auger line shape for Pd in Cu, Ag, and Au can be described in surprising detail with the above theory.[26]

The inclusion of the sp band presents a bit of a problem and is certainly necessary to describe the one-hole spectrum within the same model as the Auger spectrum. In principle, of course, the d-s hybridization is included in the Clogston-Wolff Hamiltonian in its most general form, which is

$$H = H_0 + \Delta C_{d_0}^{\dagger} C_{d_0} , \tag{18}$$

where H_0 contains the host d band and sp-band dispersion as well as the d-sp hybridization.

In this case, Γ_0^0 in Eq. (17) will be replaced by

$$\Gamma_0^0 = \sum_n \frac{\langle d \mid n \rangle^2}{\omega - \epsilon_n} , \tag{19}$$

where the n's are the eigenstates of the pure host with energies ϵ_n, and the overlap integral yields the amount of d character at site 0 in each eigenstate for the pure host.

$\text{Im}\Gamma_0^0 = \rho_{d_0}(\epsilon)$ is just the local d partial density of states for the pure host. In principle, this can be obtained from band-structure calculations of the pure host. The d-sp hybridization leads to some d density of states in the sp band which will be slowly varying with energy. In g_0^0 this will result in a weak Lorentzian-type broadening of the one-hole impurity local density in the bound-state region of the above model. This lifetime-broadened state is often referred to as a virtual bound state.

This method of including the sp band is rather tedious and relies on the accuracy of band-structure calculations. Because of this we used an approximate method which describes both the one- and two-hole impurity states rather accurately. Since the most important hybridization for the local one- and two-hole impurity density of states is that of the impurity itself we proceed as follows with the sp band. The local impurity one-hole Green's function can be written as

$$g_0^0 = \Gamma_0^0 + \Gamma_0^0 \Delta g_0^0 + \Gamma_0^0 \sum_k V_{k_d} g_k^0 , \tag{20}$$

$$g_k^0 = \phi_k^k V_{k_d} g_0^0 , \tag{21}$$

or

$$g_0^0 = \frac{\Gamma_0^0}{1 - \Gamma_0^0 \left[\Delta + \sum_k \phi_k^k V_{k_d}^2 \right]} . \tag{22}$$

Here Γ_0^0 is the pure host d-band Green's function in which we have neglected the host d-sp hybridization. The last term in Eq. (20) is a result of the impurity d-band host sp hybridization described in an Anderson manner. ϕ_k^k is then the Green's function of the sp band of the pure host neglecting the host d-sp hybridization. Within these approximations,

$$\phi_k^k = \frac{1}{\omega - \eta_k} \tag{23}$$

and

$$\Gamma_0^0 = \sum_k \frac{1}{\omega - \epsilon_{d_k}} , \tag{24}$$

where η_k describes the sp dispersion. Equation (22) in fact describes, in limiting situations, the Anderson or the above-discussed Clogston-Wolff solution. For $V_{k_d} = 0$ we obtain Eq. (16), and for $\Gamma_0^0 = 1/(\omega - \epsilon_d')$ we obtain Eq. (9) with $\epsilon_d = \epsilon_d' + \Delta$. If the sp density of states and $V_{k_d}^2$ is constant over the whole energy region of interest, we obtain

$$g_0^0 = \frac{\Gamma_0^0}{1 - (\Delta + i\pi V^2 \rho)\Gamma_0^0} . \tag{25}$$

Since this is a more realistic case than that shown in Fig. 6 and 7 we also show the results of this calculation. For the calculation we used Eq. (25) with $[\pi V^2 \rho]_{\text{av}} = 0.25$ eV, which is typical of Pt, Pd, and Ni in the noble-metal hosts. In Fig. 8 we show the host and impurity partial density of states displaying the virtual-bound-state character of the impurity state. Comparing Fig. 8 to Fig. 7 we now see that the amount of impurity character in the host band has increased considerably, which is a result of the broadening introduced. The resulting Auger spectra are shown in Fig. 9. The spectra show the same trends as those in Fig. 7, but now the amount of "band" character in the impurity Auger spectrum is considerably enhanced even for conditions such that the impurity state is well removed from the host band.
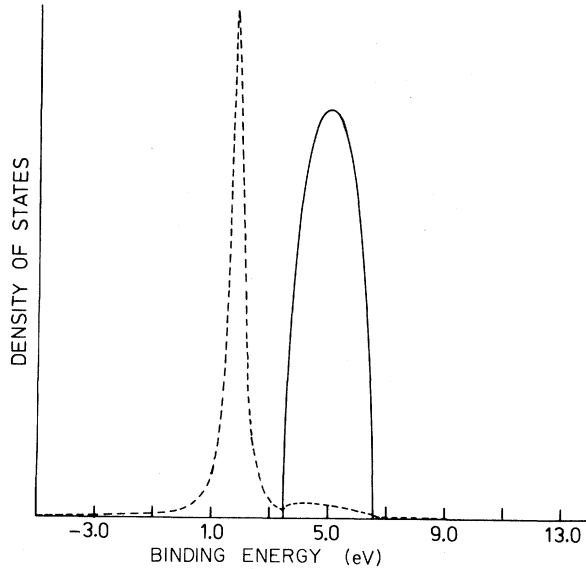
FIG. 8. Same as Fig. 6 except that now we include the interaction with the host sp band in an Anderson-type manner [Eq. (25)].

VI. DEGENERACY

Alloys for which the above analysis is particularly applicable are those in which the impurity has a full or nearly full valence d shell, such as Ni, Cu, Pd, Ag, etc., in various hosts. The interesting Auger spectra are the $L_{23}M_{45}M_{45}$ and $M_{45}N_{45}N_{45}$ spectra involving two holes in the valence d shell. Because of the orbital degeneracy Coulomb and spin-orbit interactions there are a large number of two-hole final states. For example, in Ni and Cu the $3d^8$ states reached are well described in LS coupling, resulting in the terms ^1S, ^1G, ^3P, ^1D, and ^3F. These terms are spread over a large energy range (7 eV in Cu).

Up to this point we have neglected the d-orbital degeneracy and subsequent multiplet structure. To take this into account rigorously presents quite a problem, since, although for the local two-hole state (d^8) in LS coupling, J, L, S, and M_J are good quantum numbers as the crystal-field splitting in metals is generally small.[27] This need not be true for the uncorrelated two-hole states. For small spin-orbit coupling the local and translational symmetry will not cause mixing of different spin states. So the singlets and triplets can be treated separately. To treat this problem we consider a d impurity state in cubic symmetry.

Since we are interested in the local two-particle density of states we can separate this into the contributions from the irreducible representations of the point group. In cubic point symmetry the d states transform as t_{2g} and e_g and the two-particle states span the representations $^3A_{2g}$, $^3T_{2g}$, $^3T_{1g}$, $^1A_{1g}$, $^1T_{1g}$, and ^1E_g. In Table II we show how the atomic LS states transform in cubic symmetry.

We see that it is, in fact, not rigorously correct to treat the terms independently since terms containing the same irreducible representation (IR) will mix. We can write the atomic LS wave functions in terms of the crystal-field
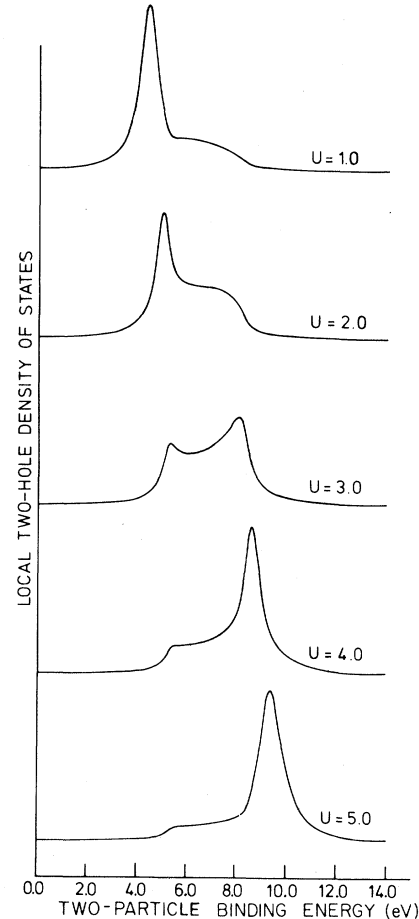

FIG. 9. Resulting Auger spectra for the local impurity density of states shown in Fig. 8.

states as given in Table III, from which we see that we must deal with at most 2×2 matrices which make the problem relatively simple. Using the same procedure as for the nondegenerate case, we can now write the two-particle function for each term as follows:

$$G_i^i(\text{IR}) = g_i^i(\text{IR}) + \sum_{j(\text{IR})} g_i^j(\text{IR}) U_{jj} G_j^i , \qquad (26)$$

$$G_j^i(\text{IR}) = g_j^i(\text{IR}) + \sum_{k(\text{IR})} g_j^k(\text{IR}) U_{kk} G_k^i , \qquad (27)$$

where the indices refer to particular LS states and IR refers to a particular irreducible representation of the point group. The sum over j and k are sums over the LS terms, containing the same IR's. In this way the Coulomb interactions U_{jj} remain diagonal and the mixing of terms is caused by the noninteracting two-particle Green's functions g_i^j which is not diagonal in LS coupling. These, however, will be diagonal in the crystal-field representation. As an example we consider the ^1E_g IR. We have

$$G_{1G}^{1G}(^1E_g) = g_{1G}^{1G}(^1E_g) + g_{1G}^{1G}(^1E_g) U_{1G} G_{1G}^{1G}(^1E_g)$$
$$+ g_{1G}^{1D}(^1E_g) U_{1D} G_{1D}^{1G}(^1E_g) , \qquad (28)$$

TABLE II. Crosses indicate the IR's spanned by the two-hole states in LS coupling.

	$^1A_{1g}$	$^1T_{1g}$	T_{2g}	^1E_g	$^3A_{2g}$	$^3T_{2g}$	$^3T_{1g}$
^1S	×						
^1D			×	×			
^1G	×	×	×	×			
^3P							×
^3F					×	×	×

$$G_{1D}^{1G}(^1E_g) = g_{1D}^{1G}(^1E_g)\, g_{1D}^{1G}(^1E_g)U_{1G}G_{1G}^{1G}(^1E_g)$$
$$+ g_{1D}^{1D}(^1E_g)U_{1D}G_{1D}^{1G}(^1E_g) , \tag{29}$$

resulting in

$$G_{1G}^{1G}(^1E_g) = \frac{\phi_G}{1 - U_G\phi_G}, \quad G_{1D}^{1G} = \frac{g_{1D}^{1G}}{(1 - g_{1D}^{1D}U_D)(1 - U_G\phi_{1G})} ,$$
$$\tag{30}$$

with

$$\phi_G = g_{1G}^{1G} + \frac{g_{1G}^{1D}g_{1D}^{1G}U_{1D}}{1 - g_{1D}^{1D}U_{1D}} . \tag{31}$$

The noninteracting two-particle Green's functions are diagonal in the crystal-field representation so that from Table III we see that

$$g_{1G}^{1G}(^1E_g) = \tfrac{4}{7}g_{t_{2g}}\otimes g_{t_{2g}} + \tfrac{3}{7}g_{e_g}\otimes g_{e_g} , \tag{32}$$

$$g_{1G}^{1D}(^1E_g) = \frac{-2\sqrt{3}}{7}(g_{t_{2g}}\otimes g_{t_{2g}} - g_{e_g}\otimes g_{e_g}) . \tag{33}$$

Here $g_{t_{2g}}$ and g_{e_g} refer to the one-particle Green's functions, the imaginary part being the partial one-particle density of states. The symbol $\otimes$ refers to a convolution.

We see from the above that if the t_{2g} and e_g density of states are equal the terms do not mix and can therefore be treated separately. Similar relations to the above can be derived for each of the IR's with the general result

$$G_{LS}^{LS}(\text{IR}) = \frac{\phi_{LS}}{1 - U_{LS}\phi_{LS}} ,$$

$$G_{LS'}^{LS}(\text{IR}) = \frac{g_{LS'}^{LS}}{(1 - g_{LS'}^{LS'}U_{LS'})(1 - U_{LS}\phi_{LS})} \tag{34}$$

TABLE III. Crystal-field components in each of the IR's of the two-hole wave function in LS coupling.

	$|t_{2g}{}^2\rangle$	$|t_{2g}e_g\rangle$	$|e_g2\rangle$
$^1S(^1A_{1g})$	$\sqrt{3/5}$	0	$\sqrt{2/5}$
$^1D(^1T_{2g})$	$\sqrt{3/7}$	$-2/\sqrt{7}$	0
$^1D(^1E_g)$	$\sqrt{3/7}$	0	$2/\sqrt{7}$
$^1G(A_{1g})$	$\sqrt{2/5}$	0	$-\sqrt{3/5}$
$^1G(^1T_{2g})$	$2/\sqrt{7}$	$\sqrt{3/7}$	0
$^1G(^1E_g)$	$-2/\sqrt{7}$	0	$\sqrt{3/7}$
$^3P(^3T_{1g})$	$1/\sqrt{5}$	$2/\sqrt{5}$	0
$^3F(^3A_{2g})$	0	0	1
$^3F(^3T_{1g})$	$2/\sqrt{5}$	$-1/\sqrt{5}$	0
$^3F(^3T_{2g})$	0	1	0

with

$$\phi_{LS} = g_{LS}^{LS} + \frac{g_{LS}^{LS'}g_{LS'}^{LS}U_{LS'}}{1 - g_{LS'}^{LS'}U_{LS'}} . \tag{35}$$

To determine the Auger spectrum we must include the Auger transition matrix elements. Denoting the transition amplitude for an LS term by A_i, the total Auger spectrum is given by

$$I(\epsilon) = \frac{1}{\pi}\sum_{\text{IR}}M_{\text{IR}}\left[\sum_i\sum_j A_iA_j\,\text{Im}\,G_i^j(\text{IR})\right] , \tag{36}$$

where M_{IR} is the total degeneracy of the irreducible representation.

We now discuss some approximations to this rather simple but tedious to work with relation. First we note that if the t_{2g} and e_g one-particle partial densities of states are the same we can treat the terms independently since all of the $G_i^j(\text{IR})$'s are zero for $i \neq j$.

If there is a difference in the t_{2g} and e_g densities of states, the ^1G intensity, which, for $3d$ and $4d$ transition metals, has the largest transition matrix element, will be redistributed over the ^1D and ^1S terms. However, since the ^1S-^1G splitting is large this redistribution of intensity will be small. Also since the ^1D-^1G splitting is small enough that the ^1D is not resolved, a redistribution of intensity here will hardly affect the spectrum. Also, the ^3F-^3P splitting intensity will be redistributed, but since the two representations $^3A_{2g}$ and $^3T_{2g}$ do not appear in any other term in ^3F, only $\tfrac{3}{7}$ of the ^3F intensity will be affected. Of this, a small amount will appear in the ^3P region of the spectrum which is not resolved from the ^1G.

In conclusion we can say that as long as the t_{2g} and e_g components of the density of states are not strongly different, we can treat the terms independently. This is certainly the case for free-electron-like hosts. Even for the noble-metal hosts it is found that the projected t_{2g} and e_g densities of states show relatively small differences. One of the real problem cases could be Au because of the large spin-orbit coupling. This can be treated in an analogous manner to that for crystal-field effects.

VII. CONCENTRATED ALLOYS

For the more concentrated alloys the situation is more complicated. Equation (4) still holds, however, so all we need is the one-hole local density of states of the component of interest. One could use the Auger spectra in these cases to test alloy calculations. For example, in a random binary alloy such as $Pd_{1-x}Ag_x$, one could try the

coherent-potential[28] approximation with a so-called single-site approximation for the alloy Hamiltonian. This approximation is equivalent in the dilute limit to the Clogston-Wolff Hamiltonian. This has recently been discussed by Drchal and Kudrnovsky.[29] We will not discuss this here, but rather we will concentrate on some qualitative aspects of the Auger spectra in more concentrated alloys. To facilitate the discussion we consider a $B_{1-x}A_x$ binary alloy, and concern ourselves with the Auger spectrum obtained following the core ionization of atom A. As shown above, the Auger spectrum is given by

$$I(\epsilon) = \alpha \frac{1}{\pi} \text{Im} \frac{g_{AA}^{AA}}{1 - U g_{AA}^{AA}} , \qquad (37)$$

where $\text{Im}(1/\pi) g_{AA}^{AA}$ is the self-convolution of the valence-band partial density of states of character belonging to atom A. As pointed out above, the most important part of this density of states is that in the region of $\epsilon_{VA} + U_A$. (ϵ_{VA} is the sole valence-hole energy of atom A that neglects hybridization.) For the Cu-Cd alloys, for example, the broadening of the ^1G Cu Auger line was due to the fact that $\epsilon_{d_{Cu}} + U_{1_G} \simeq \epsilon_{d_{Cd}}$, and the broadening was caused by a small amount of Cu d one-hole density in the region of the Cd d band owing to hybridization. The broadening observed is proportional to the amount of Cu d character in the Cd d band, which, in turn, is proportional to the number of Cd neighbors surrounding a Cu atom. This effect is clearly seen when comparing the Cu Auger spectra of Cd_3Cu and Cu_2Cd. This dependence on the nearest-neighbor coordination is expected because the hybridization is caused mainly by nearest-neighbor "hopping" integrals for d-band metals. This is rather interesting because Auger spectroscopy could then provide information about the nearest-neighbor coordination of a component of the alloy. Clearly this information can only be obtained relatively easy in the so-called split-band alloys of which alloys such as Ni, Pd, and PT with Cu, Ag, and Au are reasonable examples. Cu-Zn, Cu-Cd, Ag-Cd, Au-PT, and Cd-In alloys, just to mention a few, are also good examples.

In the split-band case we can decompose the density of states of atom A into two regions,

$$\rho_A(\epsilon) \simeq \alpha(\epsilon) \rho_A'(\epsilon) + \beta(\epsilon) \rho_B'(\epsilon) , \qquad (38)$$

as shown pictorially in Fig. 8. Here ρ_A' or ρ_B' is that portion of the density of states which is mainly of A or B character, respectively. For the case where $\rho_A'(\epsilon)$ and $\rho_B'(\epsilon)$ are well split in energy, $\beta(\epsilon)$ and $\alpha(\epsilon)$ are approximately constant and are a direct measure of the amount of hybridization. They depend strongly on the nearest-neighbor coordination. The Auger spectrum can be written as

$$I(\epsilon) = \frac{\rho_A(\epsilon) \otimes \rho_A(\epsilon)}{[1 - UF(\epsilon)]^2 + U^2 [\rho_A(\epsilon)]^* \rho_A(\epsilon)} , \qquad (39)$$

where $F(\epsilon)$ is given by

$$F(\epsilon) = P \int \frac{\rho_A(\omega) \otimes \rho_A(\omega)}{\omega - \epsilon} d\omega . \qquad (40)$$

The most important part in the self-convolution is, as pointed out above, that part which is in the energy region $2\epsilon_{VA} + U$, which for systems such as Ag-Pd (A=Pd), is that part involving

$$\alpha(\epsilon) \rho_A'(\epsilon) \otimes \beta(\epsilon) \rho_B'(\epsilon) . \qquad (41)$$

Of course, in other systems other regions may be important. The densities ρ_A' and ρ_B' can be roughly obtained from UPS or XPS after correcting for matrix-element effects. If we then normalized both regions to 1, the coefficients α and β can be crudely approximated by $\beta \simeq [N(B)/M]X$ and $\alpha = 1 - \beta$, where $N(B)/M$ is the relative number of B-types nearest neighors, and X is the amount of mixing in the dilute BA alloy.

Although this is a rather crude representation of the band structure, we present it to emphasize the point that the Auger spectrum can be very sensitive to the local surroundings of the atom. To display this, in Fig. 10 we show the calculated Auger spectra of atom A for a model density of states shown on the top of Fig. 10. The Coulomb interaction U=3 eV is taken so that $2\epsilon_{VA} + U \approx \epsilon_{VB} + \epsilon_{VA}$, as is the case for Pd-Ag alloys. The calculations are done for various values of β; β=0, $4X/12$, $6X/12$, $8X/12$, and $12X/12$, with X=0.05 using Eqs. (38) and (39). These calculations show the dependence of the Auger spectrum on the number of B nearest neighbors which could represent either various crystal structures of ordered alloys or the concentration dependence of disordered alloys. Of course, to do this properly we should also
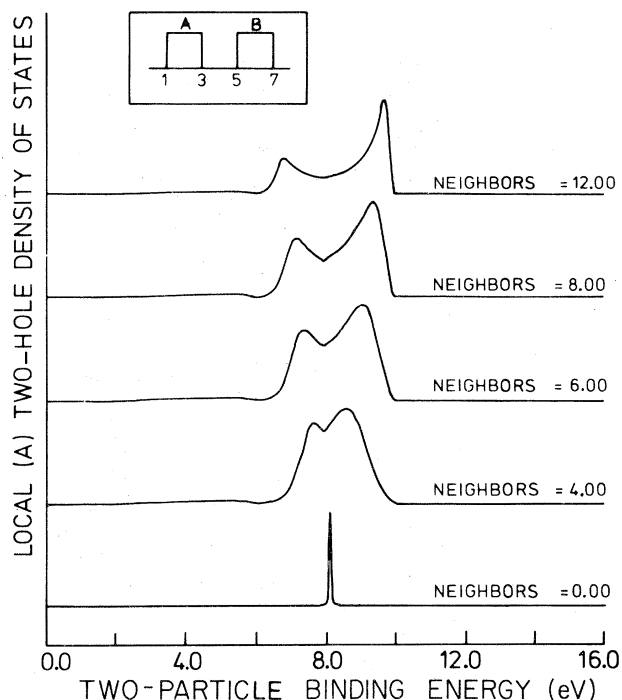

FIG. 10. Model density of states of a binary alloy (top) and the resulting Auger spectra of component A for various numbers of nearest neighbors of component B for U=3 eV.

allow the bandwidths ρ'_A and ρ'_B to vary. Here, however, we merely want to point out the strong dependence of the Auger line shape on the local surroundings.

VIII. CONCLUSIONS

In this paper we have shown how to treat the Auger-line-shape problem in alloys. We show that the line shape is strongly affected by the presence of several bands in which case the spectrum can no longer be described in terms of U/W limits since the "bandwidth" W to be used is ill defined. We developed a general theory for the Auger line shape of filled-band systems and applied it to dilute alloys with free-electron-like and Noble-metal-like hosts. Free-electron-like hosts cause a nearly-Lorentzian-broadened Auger spectrum with a width proportional to the host density of states at the energy of the impurity two-hole state. Noble-metal hosts can result in anomalous impurity Auger line shapes if the impurity *two*-hole state happens to fall inside the host-metal d band.

We also develop the theory for degenerate d-band Auger spectra and show that in most cases the Auger spectrum can be well described by treating the d^8 impurity-state terms independently. In cases where crystal-field effects and/or spin-orbit effects in the host band structure are important, this simple approximation breaks down and a theory is developed to treat these cases.

In addition, a qualitative discussion is given of the Auger line shape in more concentrated alloys, from which we conclude that Auger spectral line shapes can provide information about the nearest-neighbor surroundings of the Auger emitting atom.

ACKNOWLEDGMENTS

APPENDIX

In the treatment of an Anderson impurity we have suggested the use of an approximate relation which we derive here. The Anderson Hamiltonian for an impurity is given by

$$H = \sum_\sigma \left[\sum_k \epsilon_k C_k^\dagger C_k + \epsilon_d d^\dagger d + \sum_k V_k (C_k^\dagger d + d^\dagger C_k) + U(1-n_{d\uparrow})(1-n_{d\downarrow}) \right]$$

for an orbitally nondegenerate level. Here ϵ_d is the one-hole energy of the impurity. With the use of the Zubarev equations of motion[30] for the two-hole—state Green's function, we obtain, following Ref. 2,

$$\omega G_{dd}^{dd} = 1 + (2\epsilon_d + U)G_{dd}^{dd} + \sum_k V_k (G_{dC_k}^{dd} + G_{C_k d}^{dd}) \, ,$$

$$\omega G_{dC_k}^{dd} = (\epsilon_k + \epsilon_d)G_{dC_k}^{dd} + V_k G_{dd}^{dd} + \sum_{km} V_m G_{C_m C_k}^{dd} \, ,$$

with

$$G_{ij}^{km} = \left\langle \overline{\Psi}_g \left| C_{i\uparrow}^\dagger C_{j\downarrow}^\dagger \frac{1}{\omega - H} C_{k\uparrow} C_{m\downarrow} \right| \overline{\Psi}_g \right\rangle \, .$$

The approximation used in the text amounts to neglecting the term $G_{C_m C_k}^{dd}$, which describes the time-dependent probability amplitude that *both* holes on the impurity have moved onto host atoms. This term has mainly long-time components as compared to $G_{dC_k}^{dd}$, in which only one hole has moved and can be neglected except for energies close to the threshold. Neglecting this term we obtain

$$G_{dd}^{dd} = \frac{1}{\omega - 2\epsilon_d - U - 2\sum_k V_k^2/(\omega - \epsilon_k - \epsilon_d)} \, ,$$

where the factor of 2 is due to the fact that $G_{dC_k}^{dd} = G_{C_k d}^{dd}$ in the above approximation.

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