

Corelike nature of the Pd MVV shift in Pd-based alloys

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We present arguments based on the formal similarity of the Cini and Koster-Slater models to show that, in alloys, iVV Auger spectra that are significantly distorted from the quasiautomic form may present kinetic-energy shifts that do not correspond to the quasiautomic situation, even when the origin of the terms of the line shape is quasiautomic. By comparing measured shifts of the Pd M_5VV and $L_3M_{4,5}M_{4,5}$ true core-level spectrum in Pd-Cu alloys, we verify this conclusion in this case. The corresponding experimental shifts of Ag in Pd-Ag alloys are, however, closely related, as expected from the quasiautomic nature of the Ag MVV spectrum. In alloy studies, therefore, true core-level Auger kinetic-energy shifts should be employed.

I. INTRODUCTION

The use of shifts of core-level binding energies measured by x-ray photoelectron spectroscopy (XPS) to extract information about changes of electronic structure in transition- and noble-metal alloys is, by now, a fairly standard procedure.¹⁻¹¹ The inherent ambiguities in such analyses are best appreciated by considering the usual expression for the core-level binding-energy shift $\Delta\mathcal{B}^A(x)$ of species A in the alloy A_xB_{1-x} relative to pure metallic A ,

$$\Delta\mathcal{B}^A(x) \cong \Delta E_F^A(x) - U_d^A \delta n_d^A(x) - U_c^A \delta n_c^A(x), \quad (1)$$

where δn_d^A and δn_c^A represent the changes of d and conduction (i.e., sp -) electron counts on atom A , respectively, $\Delta E_F^A(x)$ is the relative Fermi energy,¹² and the U 's are Coulomb integrals. Since the δn 's and ΔE_F^A are *a priori* unknown, the usefulness of Eq. (1) depends on either complementary information, such as Au isomer shifts in Au-based alloys, or approximations, such as replacing ΔE_F^A by the difference in work functions, or some combination thereof.^{1-4,8}

The necessity of complementary information in extracting occupation changes from expressions like Eq. (1) has led to the suggestion that Auger kinetic-energy shifts be considered.^{9,12-16} This suggestion arises from the fact that, to a good approximation, $\Delta K_{ijk}^A(x)$, the shift of the kinetic-energy (relative to the Fermi energy) of the ijk Auger core-level transition of atom A , can be related to a core-level binding-energy shift, as in Eq. (2),

$$\Delta K_{ijk}^A(x) \cong -\Delta\mathcal{B}_k^{A(j)}(x), \quad (2)$$

where $\Delta\mathcal{B}_k^{A(j)}(x)$ is the shift in binding energy of the k core level of A when there is a hole in the j level.^{12,13,17}

That $\Delta K_{ijk}^A(x)$ has the form in Eq. (2) suggests that it may be expressed in a form analogous to that in Eq. (1),¹² and, so, could provide additional, independent, information to help in removing the ambiguities in Eq. (1). Auxiliary conditions, such as special values of x , could then complete the determination of the valence occupation changes.¹⁶ A scheme which involves employing noble-

metal Auger shifts to determine the relative Fermi energies has been proposed¹²⁻¹⁵ and applied to Au-Pd alloys,⁹ with results in agreement with independent information.

The derivations of Eq. (1) for $\Delta\mathcal{B}^A(x)$ and of the analogous equation for $\Delta K_{ijk}^A(x)$ (Ref. 12) require that the level whose shifts we are examining be much more localized spatially than the valence states (i.e., require that it be corelike in nature). In the case of Auger shifts, however, transitions whose final states are core levels often produce spectra which are either broad, partially as a result of the superposition of contributions from various terms, as in the case of the $L_{2,3}M_{2,3}M_{2,3}$ spectra of the $3d$ series¹⁸ and the $N_{6,7}O_{4,5}O_{4,5}$ spectra of Tl, Pb, and Bi,¹⁹ or are weak in intensity and, necessarily, of very high kinetic energies, as in the case of the $L_{2,3}M_{4,5}M_{4,5}$ spectra of the $4d$ series.²⁰⁻²³ For these reasons it is not common to experimentally study Auger transition involving only core levels and to measure their shifts in alloys.

The most commonly measured spectra in these materials correspond to Auger transitions in which the two final-state holes are in valence d states (i.e., iVV transitions). For metals with full initial-state d bands and for noble metals, there is convincing evidence that the iVV spectra are quasiautomic in form for the $3d$,¹⁸ the $4d$,^{24,25} and the $5d$ (Refs. 19 and 26) series. Indeed, in these systems, the final-state d -band holes have been interpreted as corelike and fully screened in the sense of the quasiautomic (QAM) model.^{17,27-29}

The evidence for the iVV spectra of metals with more than one ground-state d -band hole is more indirect. In the case of Pd, for example, comparison of the $M_{4,5}N_{4,5}N_{4,5}$ spectra and self-convolutions of XPS valence-band spectra (which reflect bandlike behavior) exhibit significant disagreement between them,^{25,30} supporting a quasiautomic interpretation. This interpretation was corroborated by the results of theoretical calculations^{25,30} indicating that the final-state holes responsible for the 1G_4 multiplets may be considered as core holes.^{20-22,25,30,31} Further support was adduced by the agreement between $3d_{3/2}$ satellite shifts and M_5VV final-state shifts of Pd in Pd-Cu alloys.³²

The interpretation of Pd final-state d -band holes as

corelike has been extended to Pd-based alloys. Model calculations applied to dilute Pd alloys indicate that the observed Auger spectra of both Pd-Cu (Ref. 33) and Pd-Ag (Refs. 34 and 35) can be explained as quasiatomic in the sense of the theories of Cini³⁶ and Sawatzky,³⁷ although there has been some controversy^{38,39} surrounding the latter alloy. This quasiatomic interpretation led to the use of the Pd Auger shifts in Pd-Cu alloys to derive thermodynamical quantities.³²

Despite the quasiatomic interpretation,⁴⁰ it is well known that the forms of the experimental Pd *MVV* Auger spectra are sensitive functions of the alloy composition^{41,42}: that is, they depend on the valence-band density of states (DOS). It is interesting, therefore, to ask to what extent the measured Pd *MVV* Auger shifts can be interpreted as arising from corelike final-state *d*-band holes and to what extent they furnish useful information complementary to that in Eq. (1).

In this paper we argue that the observed spectral sensitivity to the DOS may introduce a direct effect of the DOS on the measured shift, vitiating its utility as a binding-energy shift in the sense of Eq. (2). In order to verify this argument we present, for the first time, measurements of Pd Auger core spectra (i.e., $L_3M_{4,5}M_{4,5}$) shifts in Pd-Cu alloys and compare them with the corresponding M_5VV shifts.

In Sec. II we discuss the relation between distortions of quasiatomic line shapes and the dependence of peak energies on the DOS by exploiting the similarity between the Cini model³⁶ and the Koster-Slater model.⁴³ The results of this discussion are verified by experimentally comparing Pd M_5VV and $L_3M_{4,5}M_{4,5}$ shifts in Pd-Cu alloys in Sec. III, where we also show the agreement between the corresponding Ag shifts in Pd-Ag alloys. The conclusions are presented in Sec. IV.

II. RESONANCES AND BOUND STATES IN THE KOSTER-SLATER MODEL

Explanations of the dilute Pd *iVV* Auger spectra in Pd-Cu (Ref. 33) and Pd-Ag,^{34,35} which assume that the local Pd *d* band is full,^{36,37} relate them to the local two-hole spectral function $D(E)$, which corresponds to the imaginary part of the local two-hole Green's function,^{35-37,40} G , for two-hole binding energy $E = \mathcal{B}_i - K_{iVV}$, as in Eqs. (3),

$$G(z) = \int_{-\infty}^{\infty} dt D(t)/(z-t), \quad z = E + i\delta, \quad \delta \rightarrow 0^+ \\ = G_0(z)/[1 - UG_0(z)], \quad (3a)$$

$$D(E) = (-1/\pi)\text{Im}[G(z)] \\ = D_0(E)/\{[1 - UI_0(E)]^2 + [\pi UD_0(E)]^2\}. \quad (3b)$$

In Eqs. (3), the quantity U denotes the hole-hole Coulomb repulsion and I is the real part of G . Quantities with subscript zero denote noninteracting holes ($U=0$) so that D_0 is the self-convolution of the valence-band local DOS in the alloy.

The form of Eq. (3) is analogous to that for the Koster-Slater model⁴³ of an impurity interacting with the states of one band of a perfect crystal through a very localized repulsive potential coupling only to that band.

The analogy is exact if we interpret $D(E)$ as the one-electron DOS at the impurity site (i.e., the local DOS in the Wannier representation^{43,44}). This analogy clarifies some features of bound states and resonances we would like to discuss.

In this model, a true bound state exists at energy E_B if its energy does not overlap the continuum of band states (i.e., if it lies in the "gap") so that $D_0(E_B)=0$ and E_B is determined from the condition $F(E_B) \equiv I_0(E_B) - 1/U = 0$, as illustrated in Fig. 1(a) for a shallow and for a deep bound state. In the region of the bound state, $D(E) = A(E_B)\delta(E - E_B)$, where $A(E_B) \equiv |U^2 I_0'(E_B)|^{-1}$ and $I_0' \equiv dI_0/dE$.

If we measure energies from the center of the band and the bandwidth is 2Δ , then, for energies well removed from the band, such that $E/\Delta \gg 1$, $I_0(E) \sim N/(E - \bar{E})$, depicted by the dotted line in Fig. 1(a), where N is the integral of $D(E)$ and \bar{E} is the band centroid. In this case, $E_B \sim \bar{E} + UN$ and $D(E \sim E_B) = N\delta(E - E_B)$. Therefore, for deeply bound states, the energy and line shape are both insensitive to the details of the DOS.⁴⁵ This con-

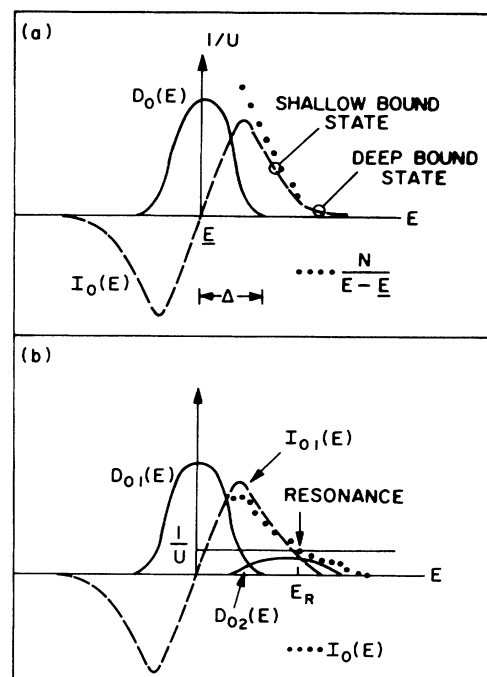


FIG. 1. (a) Schematic illustration of the bound-state condition in the Koster-Slater model. D_0 and I_0 are, respectively, the spectral function (width 2Δ) and the real part of the two-hole Green function. The dotted line represents the asymptotic form of I_0 , $N/(E - \bar{E})$. The deep and shallow bound states correspond to large and moderate values of U , respectively. (b) Schematic illustration of the resonance condition. The total spectral weight is the sum of the large (D_{01}) and small (D_{02}) components. Depicted are the total real part of the two-hole Green function (I_0) and that corresponding to the large spectral component (I_{01}). Intersection of $1/U$ with the former gives E_R , the resonance energy, and with the latter gives E_0 , the bound-state energy for just the large spectral component. When D_{02} is important, these energies may differ significantly.

clusion corresponds to the condition $\xi \gg 2\Delta$ for quasiatomic Auger spectra,^{18,36} where ξ is the Auger parameter, or the difference between uncorrelated and experimental Auger energies. In this case, the bound state is atomic in nature and $\Delta K_{iVV} = \Delta[B_i - \underline{E} - UN]$, where \underline{E} corresponds to the binding energy of two uncorrelated holes so that UN is the Auger parameter^{37,45} (self-consistent screening is neglected in this argument¹²). This situation satisfies Eq. (1) and (2) for corelike spectra.

It is well known, however, that within the Koster-Slater model, E_B is sensitive to higher moments of the DOS when the bound state approaches the band edge⁴⁶ such that $D_0(E_B) = 0$; this is illustrated for the shallow bound state in Fig. 1(a), at whose energy $I_0(E)$ differs from $N/(E - \underline{E})$. The corresponding shifts, therefore, could have direct contributions from the DOS, so that for Auger spectra, which would correspond to $\xi \geq \Delta$ in this case, ΔK_{iVV} might not necessarily reflect only the contributions in Eqs. (1) and (2). The associated spectra, however, would still arise from bound states and would appear quasiatomic. Here $A(E_B) \leq N$, so that there can still be significant spectral weight where $D_0 \neq 0$. Note that, even though we expect ξ to be within 10% of UN here,⁴⁵ the measured ξ is typically of the order of a few eV (e.g., for Pd, $\xi = 3.3$ eV for the MVV transition^{21,47}). Since the errors of the measured Auger shifts are around ± 0.10 eV, the difference between ξ and UN (which is a quasiatomic quantity) could be important for the shifts. Ideally, the shifts in each individual case should be verified by comparing with the shifts of core-level Auger transitions.

A resonance occurs when the resonance energy E_R satisfies $F(E_R) = 0$ and $D_0(E_R) \neq 0$, as illustrated by the resonance energy in Fig. 1(b). The spectral weight takes the form, for $E \sim E_R$, $D(E) \sim [A(E_R)/\pi]L(E - E_R, \Gamma(E))$, where $L(x, \gamma) \equiv \gamma/(x^2 + \gamma^2)$, and $\Gamma(E) = -\pi D_0(E)/I'_0(E)$ (Ref. 44). For this structure to have a useful interpretation as a virtual, or long-lived, state, it is necessary for $\Gamma(E)$ be small (with respect to U , for example) and to be approximately constant. Otherwise, the spectral line shape differs significantly from the quasiatomic types discussed before.

To make connection with the Pd-Ag and Pd-Cu results,^{33,34} consider, as depicted in Fig. 1(b), $D_0(E)$ as the sum of the spectral functions $D_{01}(E)$ and $D_{02}(E)$, whose widths are $2\Delta_1$ and $2\Delta_2$, whose integrals are N_1 and N_2 , and whose real parts are I_{01} and I_{02} , respectively, such that $N_1 \gg N_2$, $D_{01}(E_R) = 0$, and $D_{02}(E_R) \neq 0$ (of course, $I_0 = I_{01} + I_{02}$). In this case D_{01} would correspond to the Pd impurity spectral weight and D_{02} to the small local relic of the host band arising from $d-d$ and sp mixing.⁴⁰

If D_{02} were to vanish, then the resonance would be a bound state, and we would have the quasiatomic case discussed above. The corresponding energy E_0 is the solution of $I_{01}(E_0) = 1/U$, as manifested by the intersection of the horizontal $1/U$ line with the dashed line in Fig. 1(b). Assuming $U \geq \Delta_1$, such that $I_{01}(E_R) \gg I_{02}(E_R)$, we can expand in a Taylor's series⁴⁴ and show that $E_R \approx E_0 + I_{02}(E_0)/I'_{01}(E_0)$ and $\Gamma(E) \approx -\pi D_{02}/I'_{01}(E_0)$. To relate Γ and $E_R - E_0$, we can make the rough esti-

mate, $I_{02}(E) \sim N_2[E - \underline{E}_2]/(\Delta_2)^2 \sim 2D_{02}[E - \underline{E}_2]/\Delta_2$, where \underline{E}_2 is the centroid of D_{02} .⁴⁸

For D_{02} small, the resonance is sharp, therefore, and we can expect the observed resonance energy E_R to represent the quasiatomic situation well and the measured shifts to be useful in the sense of Eqs. (1) and (2). As D_{02} increases, however, the spectral weight becomes more distorted from that of the quasiatomic case, and the observed energy may deviate considerably from the quasiatomic, so that the shifts may not correspond to Eqs. (1) and (2) as a result of the direct influence of the DOS. It should be noted that the 25% maximum difference between ξ and UN estimated previously⁴⁵ could have a very significant effect on the shifts.

Indeed, in calculations of Auger spectra,³³⁻³⁵ different effective U 's are associated with the different multiplet terms. Since these terms sample different portions of D_{02} , we might expect different multiplet terms to shift differently, or, in other words, the whole multiplet group might not shift rigidly, despite the quasiatomic interpretation of each term.

III. EXPERIMENTAL RESULTS

The alloy samples studies were prepared according to standard metallurgical techniques reported elsewhere.⁷ The x-ray excited Auger electron spectroscopy (XAES) measurements were performed using an ion-pumped system (base pressure of $2-5 \times 10^{-10}$ Torr) with a Vacuum Science Workshop HA 100 analyzer operated in the fixed analyzer mode with a pass energy of 44 eV, which yields a Au $4f_{7/2}$ full width at half maximum of 1.5 eV. Both Al (1486.6 eV) and Mg (1253.6 eV) K_α excitations were employed and the $L_3M_{4,5}M_{4,5}$ spectra were excited by bremsstrahlung radiation^{49,50}; the anodes were operated with 15.0-mA emission current at 12.0 kV. Measured Auger energies were reproducible to within ± 0.1 eV, so that the shifts reported here are accurate to within ± 0.15 eV.

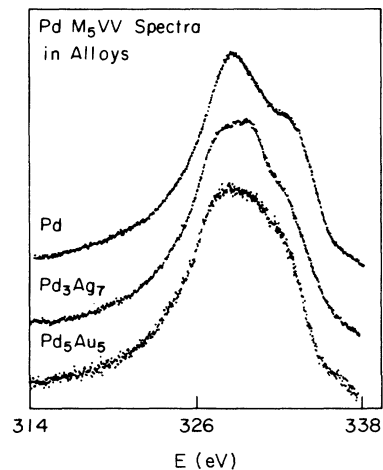


FIG. 2. Pd $M_{4,5}N_{4,5}N_{4,5}$ spectra in Pd, Pd₃Ag₇, and Pd₅Au₅. The sensitivity of the line shapes to composition and the difficulty in determining the peak energies is illustrated.

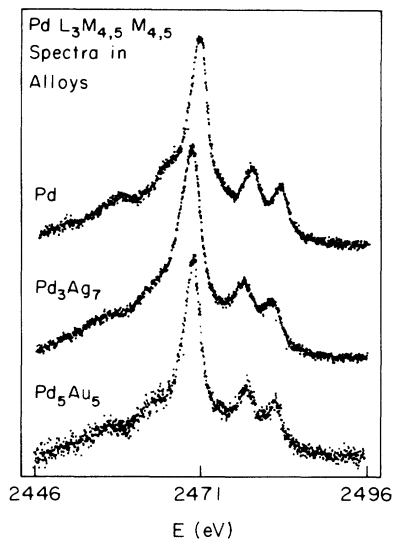


FIG. 3. Pd $L_3M_{4,5}M_{4,5}$ spectra in the same alloys as in Fig. 2. The high resolution and line-shape invariance of these core spectra are emphasized.

The samples were cleaned by argon-ion sputtering, with subsequent heating for a few minutes at temperatures between 500°C and 800°C to remove sputter damage. Contamination was monitored before and after analysis (the $L_3M_{4,5}M_{4,5}$ measurements took typically from 12 to 18 h to achieve adequate signal to noise ratios) through the carbon 1s and oxygen 1s lines.

In Fig. 2, we illustrate the sensitivity of the Pd MVV line shape by comparing intermediate compositions of Pd-Ag and Pd-Au with pure Pd. It is clear that from a practical point of view, identification and measurement of the 1G_4 peak in these alloys is quite uncertain, independent of the fundamental arguments presented above. In Fig. 3, corresponding $L_3M_{4,5}M_{4,5}$ spectra manifest the high definition of these spectra and the natural invariance of line shape.⁵¹

In Pd-Cu, the Pd MVV line shape, although distorted,^{41,42} approximates the expected quasiautomic line shape³³ much more closely than that in Pd-Ag.³⁴ As a result, measurement of the apparent position of the 1G_4 peak is possible at all compositions and, indeed, corresponding Auger shifts have been reported.³²

In Fig. 4 we present measured Pd MVV and $L_3M_{4,5}M_{4,5}$ Auger energy shifts in Pd-Cu on the abscissa and ordinate, respectively. Were the MVV shifts representative of core-levels, the corresponding data would lie on the line of slope -1 in the figure. It is clear

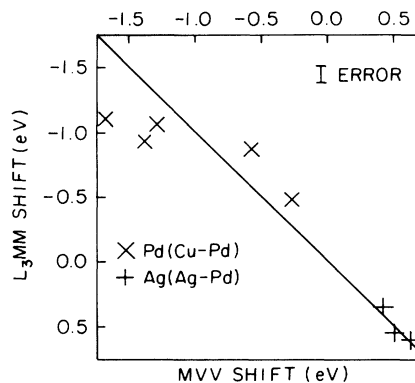


FIG. 4. $M_{4,5}N_{4,5}N_{4,5}$ shifts are plotted on the abscissa and $L_3M_{4,5}M_{4,5}$ shifts are plotted on the ordinate. Values for Pd in Pd-Cu alloys are represented by crosses and for Ag in Pd-Ag alloys are denoted by pluses. From left to right, the Pd concentrations in Pd-Cu are 0.05, 0.40, 0.30, 0.60, and 0.80. The corresponding Ag concentrations in Pd-Ag are 0.70, 0.30, and 0.05.

that this is not the case here, given our experimental error. For comparison sake, we present corresponding data for a true quasiautomic spectrum, that of Ag, in Pd-Ag: the MVV shifts obviously represent the core nature of the transition in this case.

IV. CONCLUSIONS

In conclusion, we have argued that valence-band Auger spectra in alloys, although of quasiautomic origin, can present Auger energy shifts which are not of quasiautomic nature, because of the direct influence of the valence-band DOS. As a rule of thumb, when these spectra are significantly distorted from those resulting from atomic calculations, the corresponding shifts are most suspect. In order to illustrate this point, we have measured Pd $L_3M_{4,5}M_{4,5}$ Auger shifts in Pd-Cu alloys and compared them to those of the MVV transition. It would appear that, in general, measurement of the required shifts should be made through the LMM core spectra, which are well defined.

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¹R. E. Watson, J. Hudis, and M. L. Perlman, Phys. Rev. B **4**, 4139 (1971).

²R. M. Friedman, J. Hudis, M. L. Perlman, and R. E. Watson, Phys. Rev. B **8**, 2433 (1973).

³T. S. Chou, M. L. Perlman, and R. E. Watson, Phys. Rev. B **14**, 3248 (1976).

⁴T. K. Sham, M. L. Perlman, and R. E. Watson, Phys. Rev. B **19**, 539 (1979).

⁵V. S. Sundaram, C. L. Barreto, J. D. Rogers, and G. G. Kleiman, Phys. Status Solidi B **94**, K191 (1979).

⁶G. G. Kleiman, V. S. Sundaram, J. D. Rogers, and M. B. de Moraes, Phys. Rev. B **23**, 3177 (1981).

- ⁷V. S. Sundaram, M. B. de Moraes, J. D. Rogers, and G. G. Kleiman, *J. Phys. F* **11**, 1151 (1981).
- ⁸G. K. Wertheim, R. L. Cohen, G. Crescelius, K. W. West, and J. H. Wernick, *Phys. Rev. B* **20**, 860 (1979).
- ⁹P. A. P. Nascente, S. G. C. de Castro, R. Landers, and G. G. Kleiman, *Phys. Rev. B* **43**, 4659 (1991).
- ¹⁰R. G. Jordan, Y. Jiang, M. A. Hoyland, and A. M. Begley, *Phys. Rev. B* **43**, 12173 (1991).
- ¹¹E. Choi, S.-J. Oh, and M. Choi, *Phys. Rev. B* **43**, 6360 (1991).
- ¹²G. G. Kleiman, R. Landers, S. G. C. de Castro, and J. D. Rogers, *Phys. Rev. B* **44**, 8529 (1991).
- ¹³G. G. Kleiman, *Appl. Surf. Sci.* **11/12**, 730 (1982).
- ¹⁴G. G. Kleiman, V. S. Sundaram, and J. D. Rogers, *Solid State Commun.* **39**, 1171 (1981).
- ¹⁵G. G. Kleiman, V. S. Sundaram, and J. D. Rogers, *J. Vac. Sci. Technol.* **18**, 585 (1981).
- ¹⁶T. D. Thomas and P. Weightman, *Phys. Rev. B* **33**, 5406 (1986).
- ¹⁷N. D. Lang and A. R. Williams, *Phys. Rev. B* **20**, 1369 (1979).
- ¹⁸E. Antonides, E. C. Janse, and G. A. Sawatzky, *Phys. Rev. B* **15**, 1669 (1977).
- ¹⁹J. F. McGilp, P. Weightman, and E. J. McGuire, *J. Phys. C* **10**, 3445 (1977).
- ²⁰G. G. Kleiman, R. Landers, S. G. C. de Castro, and P. A. P. Nascente, *Phys. Rev. B* **44**, 3383 (1991).
- ²¹G. G. Kleiman, R. Landers, P. A. P. Nascente, and S. G. C. de Castro, *Phys. Rev. B* (to be published).
- ²²G. G. Kleiman, R. Landers, S. G. C. de Castro, and P. A. P. Nascente, *J. Vac. Sci. Technol. A* (to be published).
- ²³G. G. Kleiman, R. Landers, P. A. P. Nascente, and S. G. C. de Castro, *Phys. Rev. B* (to be published).
- ²⁴A. C. Parry-Jones, P. Weightman, and P. T. Andrews, *J. Phys. C* **12**, 1587 (1979).
- ²⁵N. Mårtensson, R. Nyholm, and B. Johansson, *Phys. Rev. Lett.* **45**, 754 (1980).
- ²⁶R. Nyholm, K. Helenelund, B. Johansson, and S. Hörnström, *Phys. Rev. B* **34**, 675 (1986).
- ²⁷N. D. Lang and A. R. Williams, *Phys. Rev. B* **16**, 2408 (1977).
- ²⁸A. R. Williams and N. D. Lang, *Phys. Rev. Lett.* **40**, 954 (1978).
- ²⁹Even though the $N_{6,7}VV$ Auger spectra of Au and Pt have strong quasiautomatic components, the band influence in these metals is much larger than in their $3d$ and $4d$ counterparts (Ref. 26).
- ³⁰N. Mårtensson and B. Johansson, *Phys. Rev. Lett.* **45**, 482 (1980).
- ³¹N. Mårtensson, P. Hedegård, and B. Johansson, *Phys. Scr.* **29**, 154 (1984).
- ³²N. Mårtensson, R. Nyholm, H. Calén, H. Hedman, and B. Johansson, *Phys. Rev. B* **24**, 1725 (1981).
- ³³P. Weightman, H. Wright, S. D. Waddington, D. van der Marel, G. A. Sawatzky, G. P. Diakun, and D. Norman, *Phys. Rev. B* **36**, 9098 (1987).
- ³⁴M. Vos, G. A. Sawatzky, M. Davies, P. Weightman, and P. T. Andrews, *Solid State Commun.* **52**, 159 (1984).
- ³⁵P. Hedegård and B. Johansson, *Phys. Rev. Lett.* **52**, 2168 (1984); *Phys. Rev. B* **31**, 7749 (1985).
- ³⁶M. Cini, *Solid State Commun.* **20**, 605 (1976); **24**, 681 (1977); *Phys. Rev. B* **17**, 2728 (1978).
- ³⁷G. A. Sawatzky, *Phys. Rev. Lett.* **39**, 504 (1977).
- ³⁸M. Vos, D. van der Marel, G. A. Sawatzky, M. Davies, P. Weightman, and P. T. Andrews, *Phys. Rev. Lett.* **54**, 1334 (1985).
- ³⁹P. Hedegård and B. Johansson, *Phys. Rev. Lett.* **54**, 1335 (1985).
- ⁴⁰M. Vos, D. v. d. Marel, and G. A. Sawatzky, *Phys. Rev. B* **29**, 3073 (1984).
- ⁴¹P. Weightman and P. T. Andrews, *J. Phys. C* **13**, L821 (1980).
- ⁴²P. Weightman, P. T. Andrews, G. M. Stocks, and H. Winter, *J. Phys. C* **16**, L81 (1983).
- ⁴³G. F. Koster and J. C. Slater, *Phys. Rev.* **95**, 1167 (1954).
- ⁴⁴Yu. A. Izyumov, *Adv. Phys.* **14**, 569 (1965).
- ⁴⁵G. A. Sawatzky and A. Lenselink, *Phys. Rev. B* **21**, 1790 (1980).
- ⁴⁶G. G. Kleiman and M. F. Decker, *Phys. Rev. B* **17**, 924 (1978).
- ⁴⁷N. Mårtensson and R. Nyholm, *Phys. Rev. B* **24**, 7121 (1981).
- ⁴⁸G. G. Kleiman, R. J. Nelson, N. Holonyak, Jr., and J. J. Coleman, *Phys. Rev. Lett.* **37**, 375 (1976).
- ⁴⁹C. D. Wagner and J. A. Taylor, *J. Electron. Spectrosc. Relat. Phenom.* **20**, 83 (1980).
- ⁵⁰V. S. Sundaram, J. D. Rogers, and R. Landers, *J. Vac. Sci. Technol.* **19**, 117 (1981).
- ⁵¹R. Landers, P. A. P. Nascente, S. G. C. de Castro, and G. G. Kleiman, *J. Phys. Condens. Matter* (to be published).