

Determination of charge transfer in the $\text{Cu}_x\text{Pd}_{1-x}$ alloy system

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Measurements of the core-level binding energies and Auger kinetic energies of Cu and Pd in substitutionally disordered $\text{Cu}_x\text{Pd}_{1-x}$ alloys are analyzed in terms of the ‘‘correlated-charge model’’ (CCM), in which it is assumed that the charge on an atomic site is linearly dependent on its number of ‘‘unlike’’ nearest neighbors. This model has recently led to significant improvements in calculated total energies for random alloys. It is found that the measured core-level binding-energy shifts in the $\text{Cu}_x\text{Pd}_{1-x}$ alloy system are consistent with the average electrostatic potential of the random CCM lattice, given the degree of charge transfer predicted by *ab initio* calculations. We show experimentally that final-state relaxation energy shifts are small. [S0163-1829(97)01443-4]

I. INTRODUCTION

Core-level photoelectron binding energies E_b and Auger kinetic energies E_k are sensitive to the local electronic structure and have long been used to infer chemical information.^{1,2} One physical process giving rise to chemical shifts in molecules and solids is the transfer of charge between the constituent atoms. There is justified reluctance for solid-state physicists to speak of ‘‘charge transfer’’ as this does not constitute an observable. Nonetheless the concepts of electronegativity and ionicity have had great historical importance in chemistry^{3,4} and can provide a compact description of electronic structure and bonding. The quest for an *ab initio* description of the physical and electronic structure of disordered systems has recently stimulated renewed interest in the Madelung problem and the determination of local charges in alloys.⁵ It is therefore timely to reconsider the validity of the charge-transfer interpretation of binding-energy shifts. In the present work we analyze chemical shifts for the $\text{Cu}_x\text{Pd}_{1-x}$ system which forms random substitutional alloys across the entire composition range.

II. EXPERIMENTAL DATA

Core-level binding energy shifts are related to both changes in the ground-state electronic structure and to changes in relaxation energy. This is usually expressed

$$\Delta E_b = \Delta V - \Delta E_R, \quad (1)$$

where V is the ground-state core potential and E_R is the core-hole relaxation energy. The Auger parameter α , defined as the sum of a core-level binding energy and a core-core-core Auger energy,⁶ provides an estimate of the final-state contributions to chemical shifts:

$$\Delta \alpha = \Delta E_b + \Delta E_k \approx 2\Delta E_R. \quad (2)$$

To determine Auger parameter shifts, and so estimate relaxation shifts, we have measured both core-level photoelectron and core-core-core Auger spectra for $\text{Cu}_{0.8}\text{Pd}_{0.2}$, $\text{Cu}_{0.5}\text{Pd}_{0.5}$, and the pure elements. Substitutionally disordered alloy specimens were prepared by melting weighed quantities of

high-purity components in an argon atmosphere followed by rapid quenching. X-ray-excited photoelectron and Auger spectra were obtained using the Scienta ESCA 300 spectrometer at the RUSTI facility at Daresbury Laboratory.

Measured Cu $2p$ binding energy shifts for our specimens were consistent with previous work^{7,8} as shown in Fig. 1. It has previously been observed⁸ that the asymmetry of the Cu $2p$ photoelectron line is independent of alloy composition, suggesting that the Cu $3d$ partial density of states lies below the Fermi energy at all compositions, in agreement with the results of electronic structure calculations⁹ and with valence-band photoelectron spectroscopy.¹⁰ The asymmetry in the $3d$ photoelectron line is pronounced in Pd metal on account of the large density of unfilled states at the Fermi level. As Cu is introduced the Pd d band becomes increasingly bound and it has been shown⁸ that the Pd core-level asymmetry decreases monotonically. Beyond $x \sim 0.6$ the d band lies below the Fermi level⁷⁻⁹ and the Pd $3d$ lines exhibit low asymmetry.⁸ The apparent peak position of highly asymmetric core lines depends on both the spectrometer resolution and the asymmetry parameter¹¹ and so the observed chemical shifts of the Pd $3d$ lines in $\text{Cu}_x\text{Pd}_{1-x}$ contain a spurious

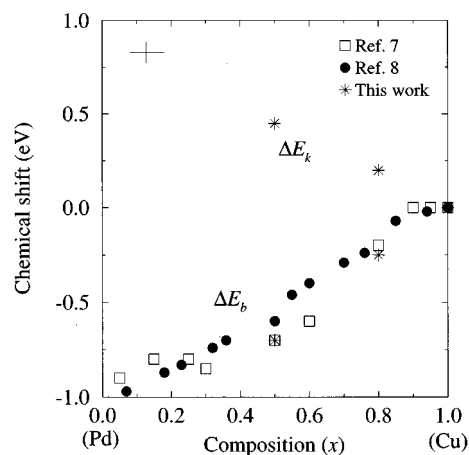


FIG. 1. Core-level binding-energy shifts ΔE_b for the Cu $2p$ level and Auger shifts ΔE_k for the Cu $L_{23}M_{23}M_{23}$ transition in $\text{Cu}_x\text{Pd}_{1-x}$ alloys relative to pure Cu.

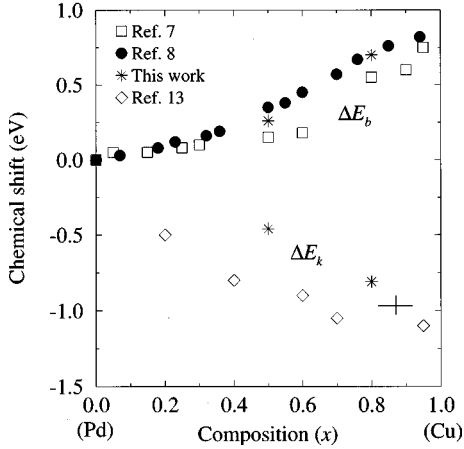


FIG. 2. Core-level binding-energy shifts ΔE_b for the Pd $3d$ level and Auger shifts ΔE_k for the Pd $L_3M_{45}M_{45}$ transition in $\text{Cu}_x\text{Pd}_{1-x}$ alloys relative to pure Pd.

instrumental contribution. Martensson *et al.* quantified this effect and presented their experimental data in corrected form.⁸ When the Martensson correction is applied to our Pd $3d$ binding energy measurements we obtain good agreement with their results, as demonstrated in Fig. 2. The measurements of Sundaram *et al.*⁷ were obtained with an unmonochromated excitation source and so require a larger correction. For this reason application of the Martensson correction to the data of Ref. 7 systematically underestimates the Pd $3d$ binding energy shifts, as shown in Fig. 2.

Cu and Pd Auger shifts are shown in Figs. 1 and 2, respectively. The Cu $L_3M_{23}M_{23}$ Auger shifts measured in the present work for $\text{Cu}_{0.8}\text{Pd}_{0.2}$ and $\text{Cu}_{0.5}\text{Pd}_{0.5}$ were found to be similar to previous measurements of the corresponding $L_3M_{45}M_{45}$ shifts,^{8,13} confirming the highly localized nature of the Cu $M_{45}M_{45}$ states. The Pd $L_3M_{45}M_{45}$ Auger shifts measured here for $\text{Cu}_{0.8}\text{Pd}_{0.2}$ and $\text{Cu}_{0.5}\text{Pd}_{0.5}$ were found to be smaller than reported previously.¹² The reason for this is not apparent. We obtained Auger parameter shifts for $\text{Cu}_{0.8}\text{Pd}_{0.2}$ and $\text{Cu}_{0.5}\text{Pd}_{0.5}$ relative to pure Cu of -0.05 and -0.25 eV, respectively, and of -0.11 and -0.20 eV, respectively, relative to pure Pd. These observations suggest that relaxation energy shifts do not make a major contribution (≤ 0.1 eV) to the photoelectron binding-energy shifts. The measured chemical shifts in E_b , E_k , and α for $\text{Cu}_{0.8}\text{Pd}_{0.2}$ and $\text{Cu}_{0.5}\text{Pd}_{0.5}$ relative to the corresponding elemental metals are summarized in Table I.

III. ELECTROSTATICS IN DISORDERED SYSTEMS

Over the last decade band-structure methods based on the coherent-potential approximation (CPA), in which atoms of

elements A and B are embedded in an effective medium, have proved the best available description of the electronic structure of random substitutional alloys.¹⁴ The CPA is a single-site theory treating all A and separately all B atoms as equivalent, and in this limit the Madelung energy vanishes by construction. Since the charge on an atom in a disordered alloy is likely to vary with local environment there is some doubt regarding the accuracy of CPA total energies and hence calculated structural properties for alloys with non-negligible charge transfer.⁵

In ordered systems the electrostatic energy is well defined and there is no need to quantify charge transfer in order to calculate the total energy. In disordered systems the best means currently available for evaluating the Madelung contribution to the total energy is to calculate the electrostatic energy of a substitutionally disordered array of point charges where the charge on each site is determined by a model. Chemical wisdom suggests that an atom surrounded by all “like” atoms will be approximately neutral, while an atom bonded to all “unlike” atoms will experience the maximum possible charge transfer. Magri *et al.*¹⁵ have proposed a model where Δq^i , the net charge on the atom at site i , is linearly proportional to N_u , the number of unlike neighbors around that site:

$$\Delta q^i = 2\lambda N_u S^i, \quad (3)$$

where the occupation variable S^i is $-1(+1)$ if site i is occupied by an $A(B)$ atom, and λ determines the ionicity. Thus the *charges* in a disordered system are correlated even when the *site occupations* are truly random. We refer to Eq. (3) as the “correlated-charge model” (CCM).

Using point-charge electrostatics Magri *et al.*¹⁵ showed that within the CCM the Madelung energy of a disordered system can be comparable to that for ordered structures. Extensions of the standard CPA have subsequently been devised^{16,17} to provide a correction for the neglect of charge correlation. In the charge-correlated CPA (cc-CPA)¹⁷ the charge on a site is assumed to be a function of N_u , although no assumption of linearity is made. The cc-CPA gave a dramatic improvement in the formation energies of several alloys. In addition it gave self-consistently determined charges that were linear in N_u and had a gradient independent of composition. These results lend great support to the CCM.

In core-level photoelectron spectroscopy the effects of disorder are manifest in the electrostatic *potential* rather than the *energy*. Within the CCM the average charge on the $A(B)$ atoms is¹⁸

$$\overline{\Delta q}^{A(B)} = 2\lambda(1 - c^{A(B)})Z_1 S^{A(B)}, \quad (4)$$

TABLE I. Photoelectron (ΔE_b), Auger (ΔE_k), and Auger parameter ($\Delta\alpha$) shifts for $\text{Cu}_{0.8}\text{Pd}_{0.2}$ and $\text{Cu}_{0.5}\text{Pd}_{0.5}$. All measurements are with respect to the corresponding elemental metal and are in units of eV.

	Cu shifts			Pd shifts		
	$\Delta E_b(2p)$	$\Delta E_k(L_3M_{23}M_{23})$	$\Delta\alpha$	$\Delta E_b(3d)$	$\Delta E_k(L_3M_{45}M_{45})$	$\Delta\alpha$
$\text{Cu}_{0.8}\text{Pd}_{0.2}$	-0.25	0.20	-0.05	0.70	-0.81	-0.11
$\text{Cu}_{0.5}\text{Pd}_{0.5}$	-0.70	0.45	-0.25	0.26	-0.46	-0.20

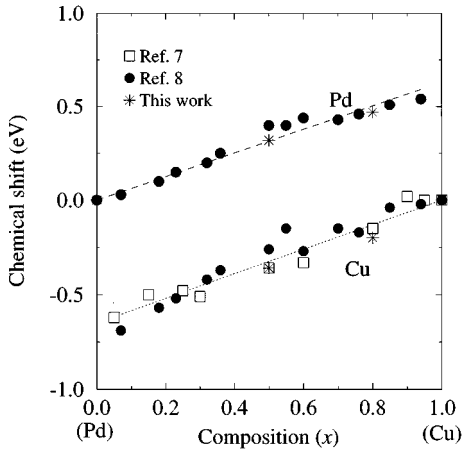


FIG. 3. Cu $2p$ and Pd $3d$ binding-energy shifts in $\text{Cu}_x\text{Pd}_{1-x}$ with Fermi-level shifts removed.

where $c^{A(B)}$ is the fractional composition of $A(B)$ atoms and Z_1 is the number of atoms in the nearest-neighbor shell. For all crystal structures and compositions there resides on average a charge $-\overline{\Delta q}^{A(B)}$ in the nearest-neighbor shell of each $A(B)$ site, while all subsequent shells are on average charge neutral.¹⁸ This corresponds to unit Madelung constant and so the average Madelung potential \overline{V}^M is

$$\overline{V}^{MA(B)} = -14.4 \frac{\overline{\Delta q}^{A(B)}}{R} = -28.8 \frac{\lambda}{R} (1 - c^{A(B)}) Z_1 S^{A(B)}. \quad (5)$$

If the nearest-neighbor distance R is in Å and $\overline{\Delta q}$ is in units of e , the electronic charge, then \overline{V}^M is in Volts. From electronic-structure calculations Lu *et al.*¹⁹ have obtained $\lambda = 5.5 \times 10^{-3}$ for CuPd alloys, corresponding to an average charge transfer of 0.07 electrons from Pd to Cu in $\text{Cu}_{0.5}\text{Pd}_{0.5}$.

In summary the CCM requires the average charge transfer and hence ΔV to vary linearly with composition, and the calculated λ of Lu *et al.*¹⁹ predicts the magnitude of these shifts. These predictions will now be tested against the experimental results from electron spectroscopy.

IV. ANALYSIS

Experimental binding energies for solids are usually measured with respect to the Fermi level, while the zero of potential in the CCM corresponds to the ‘‘crystal zero’’²⁰ of the solid. It is therefore necessary to subtract from the measured shifts the contribution due to the variation in Fermi energy with alloy composition. The role of Fermi-level shifts in determining binding energy and Auger shifts has been stressed by Kleiman *et al.*¹² Addition of Cu to pure Pd is expected to effect little change in the Fermi energy until the Pd d band is filled. Beyond this point additional electrons must be accommodated in the rather flat sp band, causing a slight increase in Fermi energy with x . This argument is borne out by the results of Winter *et al.*⁹ who found a variation in Fermi energy of ~ 0.35 eV across the composition range in $\text{Cu}_x\text{Pd}_{1-x}$ alloys.²¹ The experimental binding-energy shifts are plotted in Fig. 3 with the Fermi-level shifts⁹ removed.

Assuming the contributions to V arising from the nucleus

and the core electrons are chemically invariant, ground-state shifts can be written

$$\Delta V = \Delta V^v + \Delta V^M, \quad (6)$$

where V^v is the contribution due to the valence charge density, and α^M is the Madelung constant. In this way we obtain the familiar ‘‘potential model’’^{1,2,22}

$$\Delta V = \Delta q \left(k - 14.4 \frac{\alpha^M}{R} \right), \quad (7)$$

where k is the contribution to the core potential per valence electron.²²

With core-level photoelectron spectroscopy one observes for disordered systems a superposition of core spectra representing the possible configurations in a random system.¹⁸ Measured core-level binding energies are therefore related to the average charges $\overline{\Delta q}$ of Eq. (4).

A. Cu shifts

The Cu $2p$ binding energy shifts in $\text{Cu}_x\text{Pd}_{1-x}$ are well represented by

$$\Delta E_b(x) = -0.65(1-x) \quad (8)$$

given by the dotted line in Fig. 3. Since relaxation shifts are small, $\Delta E_b \approx \Delta V$ and we obtain

$$2\lambda Z_1 = \frac{-0.65}{k - 14.4\alpha^M/R}. \quad (9)$$

An estimate of k for the free atom is given by 14.4 times $\langle 1/r_v \rangle$, the expectation value of the radius operator for the valence shell of the free atom.²² For Cu this gives a value of 10.6 eV. A detailed study of k has been performed for the Cu atom using atomic structure calculations, and $k = 7.7$ eV was obtained.²³

While atomic structure calculations allow k to be determined for free atoms we must consider possible solid-state effects on the core potential. Although relaxation energy shifts between a wide range of metals and their corresponding free atoms have been calculated quite accurately using a simple potential model with atomic parameters,²⁴ it is well known that the compression of the valence charge density within the Wigner-Seitz radius increases $\langle 1/r_v \rangle$ and hence $k^{\text{solid}} = \gamma k$, where $\gamma > 1$.^{25,22} An empirical determination of k^{solid} from experimental core-level binding-energy shifts between free atoms and metals is hampered by the need to account for the surface dipole potential of the metal²⁰ which is usually not precisely known. Calculations which neglect both valence compression and the surface dipole tend to reproduce experimental metal-atom binding energy shifts to an accuracy of ~ 1 eV,^{20,24} suggesting the near cancellation of these effects. This implies that the compression effect on the core potential amounts to several eV. An upper bound for γ may be established by comparing $\langle 1/r_v \rangle$ obtained for the atomic valence wave function with its value for a renormalized wave function truncated at the Wigner-Seitz radius, as suggested by Watson *et al.*²⁵ Following this approach, Gregory *et al.* obtained²⁶ $\gamma = 1.83$ for Cu, giving $k^{\text{solid}} = 14.1$ eV. Finally a touching sphere model of the solid yields k^{solid}

$\approx 14.4 \times 2/R = 11.2$ eV. This estimate lies roughly midway between the atomic and renormalized values for Cu and we use this value.

Given k , Eq. (9) allows the determination of the charge-transfer parameter λ for the $\text{Cu}_x\text{Pd}_{1-x}$ alloy system. We obtain $\lambda = 4.9 \times 10^{-3}$, corresponding to an average charge transfer of 0.06 electrons from Pd to Cu for the $x=0.5$ composition. This empirically determined λ is in excellent agreement with the value of 5.5×10^{-3} obtained by Lu *et al.*¹⁹ However this degree of agreement must be regarded as fortuitous given the uncertainty in the determination of k for the solid state. Since k and $14.4\alpha^M/R$ are of opposite sign and similar magnitude the overall error due to uncertainty in k is fundamentally large. If we take the most extreme estimates of k^{solid} we obtain $0.003 < \lambda < 0.010$. Nonetheless, the absolute scale of the charge transfer deduced from experiment is consistent with *ab initio* calculations. Also the linearity of V against x is demonstrated both experimentally and theoretically.

B. Pd shifts

As discussed in Sec. II there is experimental^{8,10} and theoretical⁹ evidence that the Cu d band in $\text{Cu}_x\text{Pd}_{1-x}$ alloys lies below the Fermi energy for all concentrations, while the Pd d band is unfilled for $x < 0.6$. Thus one may expect the Pd chemical shifts to be related to intra-atomic valence configuration changes²⁰ as well as interatomic charge transfer. Since the parameter k for free atoms distinguishes strongly between d and sp valence electrons the formalism used to derive Eq. (7) should be generalized in the manner shown previously by Kleiman and Landers²⁷ and also by the present authors.²⁴ For disordered alloys it is necessary to account for the dependence of d and sp occupancies on *local* as well as *global* composition. Since Kleiman and Landers have shown²⁷ that x-ray photoelectron spectroscopy and Auger shifts in the generalized formalism have a nonlinear dependence on the d and sp occupancy changes, one must not assume that the formalism in Refs. 24 and 27 relates the *site-averaged* chemical shifts to the *site-averaged* occupation changes in disordered alloys.

With the generalized formalism^{27,24} we no longer expect a necessarily linear dependence of ΔE_b with concentration, nor should the relation $\Delta\alpha \approx 2\Delta E_R$ necessarily hold. However an approximately linear dependence of ΔE_b on x can be seen in Fig. 3, suggesting that k_d and k_s for Pd may be similar in the solid state, as Gregory *et al.* have found²⁶ for a number of transition metals. The experimental Pd binding energy shifts are consistent with estimates of charge transfer discussed above, but, given the uncertainty in determining solid-state potential model parameters and in applying the generalized formalism to disordered alloys, further analysis of the Pd shifts is not justified.

It should be noted that although the Cu d band is well below the Fermi-level hybridization ensures that these states do not have pure d character and so formally Cu does not have a d occupancy of 10. It is hoped that in the future a better knowledge of the k parameters and of the dependence of configuration changes on local composition in disordered alloys will allow analysis of both the Cu and Pd chemical shifts in some kind of generalized Kleiman-Landers model.

V. SUMMARY

An interpretation of core-level shifts in $\text{Cu}_x\text{Pd}_{1-x}$ alloys in terms of charge transfer between the constituent atoms has been performed. The Auger parameter was used to estimate the importance of relaxation energy changes with composition. Final-state shifts were found to be small for this alloy system and were subsequently neglected. Shifts in the ground-state potential were found to follow a linear variation with alloy composition as predicted by point-charge electrostatics and the correlated-charge model. The absolute scale of charge-transfer was found to be modest (on the scale of hundredths of electrons per atom) and in accord with results of *ab initio* calculations. This study demonstrates the validity of the simple charge-transfer picture for the $\text{Cu}_x\text{Pd}_{1-x}$ alloy system. The semiquantitative nature of the potential model and the difficulties in determining accurate model parameters for the solid state have been discussed.

¹K. Seigbahn *et al.*, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1969).

²U. Gelius, *Phys. Scr.* **9**, 133 (1974).

³L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1935).

⁴J. C. Phillips, *Rev. Mod. Phys.* **42**, 317 (1970).

⁵See, for example, A. Zunger in *Statics and Dynamics of Alloy Phase Transformations*, edited by P. E. A. Turchi and A. Gonis (Plenum, New York, 1994), p. 361; D. D. Johnson and F. J. Pinski, in *Metallic Alloys: Experimental and Theoretical Perspectives*, edited by J. S. Faulkner and R. G. Jordan (Kluwer, Dordrecht, 1994), p. 149.

⁶C. D. Wagner, *Faraday Discuss. Chem. Soc.* **60**, 291 (1975).

⁷V. S. Sundaram, M. B. de Moraes, J. D. Rogers, and G. G. Kleiman, *J. Phys. F* **11**, 1151 (1981).

⁸N. Martensson, R. Nyholm, H. Calen, J. Hedman, and B. Johans-

son, *Phys. Rev. B* **24**, 1725 (1981).

⁹H. Winter, P. J. Durham, W. M. Temmerman, and G. M. Stocks, *Phys. Rev. B* **33**, 2370 (1986).

¹⁰T.-U. Nahm, M. Han, S.-J. Oh, J.-H. Park, J. W. Allen, and S.-M. Chung, *Phys. Rev. B* **51**, 8140 (1995).

¹¹G. K. Wertheim, in *Photoemission in Solids*, edited by M. Cardona and L. Ley (Springer, Berlin, 1978).

¹²G. G. Kleiman, R. Landers, S. G. C. de Castro, and J. D. Rogers, *Phys. Rev. B* **44**, 8529 (1992).

¹³G. G. Kleiman, R. Landers, S. G. C. de Castro, and P. A. P. Nascente, *Surf. Sci.* **287/288**, 794 (1993).

¹⁴See, for example, B. L. Gyorffy, D. D. Johnson, F. J. Pinski, D. M. Nicholson, and G. M. Stocks, in *Alloy Phase Stability*, edited by G. M. Stocks and A. Gonis (Plenum, New York, 1994), p. 293.

¹⁵R. Magri, S. H. Wei, and A. Zunger, *Phys. Rev. B* **42**, 11 388 (1990).

- ¹⁶I. A. Abrikosov, Yu. H. Vekilov, P. A. Korzhavyi, A. V. Ruban, and L. E. Shilkrot, *Solid State Commun.* **83**, 867 (1992).
- ¹⁷D. D. Johnson and F. J. Pinski, *Phys. Rev. B* **48**, 11 553 (1993).
- ¹⁸R. J. Cole, N. J. Brooks, and P. Weightman, *Phys. Rev. Lett.* **78**, 3777 (1997); R. J. Cole and P. Weightman, *J. Phys.: Condens. Matter* **9**, 5609 (1997).
- ¹⁹Z. W. Lu, S. H. Wei, and A. Zunger, *Phys. Rev. B* **45**, 10 314 (1992).
- ²⁰R. E. Watson, M. L. Perlman, and J. F. Herbst, *Phys. Rev. B* **13**, 2358 (1976); A. R. Williams, and N. D. Lang, *Phys. Rev. Lett.* **40**, 954 (1978).
- ²¹While there has been some discussion regarding the accuracy of the Pd local DOS for Cu-rich CuPd alloys presented in Ref. 9 [see, for example, Tschang-Uh Nahm *et al.*, *Phys. Rev. Lett.* **70**, 3663 (1993); **72**, 794 (1994); P. Weightman *et al.*, *ibid.* **72**, 793 (1994), references therein] the calculated Fermi levels are expected to be reliable.
- ²²T. D. Thomas and P. Weightman, *Phys. Rev. B* **33**, 5406 (1986).
- ²³Yu. Kucherenko, A. Ya. Yaresko, G. Cubiotti, P. Weightman, and R. J. Cole, *J. Electron Spectrosc. Relat. Phenom.* **76**, 333 (1995).
- ²⁴R. J. Cole, N. J. Brooks, P. Weightman, and J. A. D. Matthew, *Phys. Rev. B* **52**, 2976 (1995).
- ²⁵R. E. Watson, J. Hudis, and M. L. Perlman, *Phys. Rev. B* **4**, 4139 (1971); T. K. Sham, M. L. Perlman, and R. E. Watson, *Phys. Rev. B* **19**, 539 (1979).
- ²⁶D. A. C. Gregory, A. D. Laine, P. S. Fowles, A. Takahashi, and P. Weightman, *J. Phys.: Condens. Matter* **5**, 3843 (1993).
- ²⁷G. G. Kleiman and R. Landers, *J. Electron Spectrosc. Relat. Phenom.* **76**, 319 (1995).