

## Electron-spectroscopic studies of the $\text{Cu}_x\text{Pd}_{1-x}$ alloy system: Chemical-shift effects and valence-electron spectra

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The valence- and core-electron spectra have been investigated for a series of  $\text{Cu}_x\text{Pd}_{1-x}$  alloys by means of ESCA (electron spectroscopy for chemical analysis). In the dilute limits a subtraction method is applied to derive the contribution of the low-concentration components to the valence-electron spectra. The Pd core-line asymmetry scales with the local palladium density of states at the Fermi level, and it is heavily reduced in the dilute palladium limit. For the Pd  $M_{45}N_{45}N_{45}$  Auger spectrum a bandlike contribution is identified in addition to the dominating quasiatomic part. Special attention is paid to the chemical shifts of the Pd and Cu core levels as a function of alloy concentration. From these and the two-hole Auger final-state energy shifts various thermochemical data are derived and compared with experiment. In general, a good agreement is obtained, suggesting that ESCA calorimetry might become a very rapid and useful method for thermochemical investigations.

### I. INTRODUCTION

Electron spectroscopy has proved to be a powerful tool for studying the electronic structure of alloys and intermetallic compounds.<sup>1-6</sup> The most direct information can be obtained from the valence-electron spectra which will give details about the valence-band structure of the alloy. However, the core-level spectra also can give valuable information about the properties of the alloy. For instance, a metallic system always gives rise to asymmetric core-electron lines<sup>7-11</sup> due to shake-up processes in the conduction band. This core-line asymmetry has been shown to depend on the local density of states at the Fermi level of the core-ionized atom.<sup>12</sup>

A most important property of the electron spectrum is that the core lines show energy shifts which depend on the chemical environment of the atom. Especially in molecular systems this property has been utilized for the discussion of numerous chemical problems. For alloys, however, the situation has been somewhat more unclear. Firstly, the shifts are comparatively small, and secondly, one has found no direct and simple relation between the chemical shifts and properties such as charge transfer or electronegativity differences. Furthermore, the concept of charge transfer is particularly difficult to define in

a natural way for an alloy. A charge transfer will certainly affect the core-level binding energy due to the accompanying change in the Coulomb potential felt by the core electrons. But in addition to this, the core-line energies measured by ESCA (electron spectroscopy for chemical analysis) equally as well reflect the property of the hole state produced by the ionization, i.e., the property of the final state. The final state, involving the relaxation and the screening due to the surrounding medium, will therefore also depend on the atomic composition and accordingly must be considered in the analysis of the chemical shift. This influence of the final state has not always been taken into account in the interpretation of the chemical shifts. (Notice that we use the concept of chemical shift as a synonym for the measured shift.)

Recently a method for obtaining core-level binding energies in pure metals was devised by Mårtensson and Johansson.<sup>13,14</sup> Within the framework of this method a simple description of chemical shifts in alloys can be also given. It can be shown that there is a close relation between chemical shifts and alloy heat-of-formation data.<sup>14</sup> Recently the model was applied to the chemical shifts of some forty dilute alloys.<sup>15</sup> The alloy heat-of-formation data were obtained from Miedema's semi-empirical scheme.<sup>16-18</sup> A most promising agree-

ment between experimental shifts and shifts calculated from the semiempirical thermochemical data was obtained. Also, a recent experimental study of the chemical shift of the Pd  $3d_{5/2}$  core level in  $\text{Pd}_x\text{Ag}_{1-x}$  alloys has shown that very accurate heat-of-formation data over the whole concentration range can be extracted.<sup>19</sup>

The above-mentioned formulation for the interpretation of the chemical shift does not provide any direct microscopic information about the electronic structure of the alloy. Instead it relates one type of measurement (chemical shift) to another (heat of formation). However, an important virtue of this method is that it directly points to the various terms which contribute to the chemical shifts. Furthermore, it seems to provide a means by which thermochemical data can be extracted from the relatively easily obtained core-level binding-energy shifts. One aim of this paper is to investigate this possibility for the  $\text{Cu}_x\text{Pd}_{1-x}$  alloy system.

Copper and palladium form a system of complete solid solubility. It is therefore a most suitable case for studying alloying effects. In a previous Letter<sup>20</sup> we discussed the properties of the Pd  $M_{45}N_{45}N_{45}$  Auger spectrum and the shake-up structures accompanying the  $M_4$  and  $M_5$  lines. The shake-up satellite and the  $N_{45}N_{45}$  Auger final state were found to show the same chemical shift as a function of Cu concentration for a set of  $\text{Cu}_x\text{Pd}_{1-x}$  alloys. This fact was taken as mutual support for the localized double-hole character of both the Auger final state ( $4d^8$ ) and the final state corresponding to the core-level shake-up satellite ( $3d^94d^9$ ). In this paper we will focus on the valence-band structure, its relation to the core-line asymmetry and on the chemical-shift effects. We will discuss the shifts of the photoelectron lines as well as the Auger-electron shifts.

The paper is organized as follows. In Sec. II we account for some of the experimental details. The experimental valence-band spectra and core-line asymmetries for the  $\text{Cu}_x\text{Pd}_{1-x}$  alloys are presented and discussed in Sec. III. In Sec. IV we discuss the chemical shifts of single-hole states as well as of double-hole states and their relation to thermochemical data. Finally, in Sec. V, a discussion of the obtained results is given.

## II. EXPERIMENTAL

For the copper-palladium system, solid solutions with any concentration between pure copper and pure palladium can be obtained. Below 600°C, the phase diagram contains stable ordered structures based on the stoichiometric compositions  $\text{PdCu}_3$

and  $\text{PdCu}$ . For higher temperatures, a disordered fcc structure is stable with equal probability for copper and palladium atoms to occupy the lattice points.

For this investigation, samples of disordered CuPd solid solutions were prepared with concentrations close to 10, 20, . . . , 90 at. % copper. The preparation involved induction melting of the constituents under argon atmosphere in quartz tubes with a subsequent rapid cooling through the two-phase region and a careful homogenization procedure.

For the disordered fcc phase of CuPd, the lattice constant increases monotonously with increasing content of palladium.<sup>21</sup> The samples were analyzed in an x-ray diffractometer and the concentrations were calculated from the obtained values of the lattice constants. The concentration values given in this paper are based on mass determinations before and after the melting and on the x-ray diffraction data. The error is estimated to be smaller than 4%.

According to the phase diagram, a transition to ordered phases is possible in the regions 7–29 at. % Pd and 30–55 at. % Pd. The general conclusion from the analysis of the x-ray diffraction patterns is that the deviations from the disordered structure are small also in these concentration regions.  $\text{Cu}_{60}\text{Pd}_{40}$  is probably an exception since the diffraction pattern shows a faint reflection indicative of a cubic structure and narrow fcc peaks indicating an increased ordering of the crystal structure.

As will be discussed below, the core-electron spectrum from a CuPd alloy contains several features which are very sensitive to the composition of the sample. This is true for the peak position, i.e., the electron binding energy, as well as for the peak intensity and the peak asymmetry. In particular, the Pd  $3d_{5/2}$  and Cu  $2p_{3/2}$  binding energies have been analyzed, and they reflect the composition of the samples in a very sensitive way. Also, the variation of the palladium-to-copper core-line intensity ratio follows the composition of the sample. This variation is mainly determined by the bulk composition as derived from x-ray diffraction data or from data in the preparation procedure. A detailed analysis of the intensities requires that such effects as the surface enrichment in the outermost atomic layers, the different photoelectric cross sections, and the different electron escape depths are taken into account. However, a very smooth variation of the Pd  $3d_{5/2}$  to Cu  $2p_{3/2}$  intensity ratio was found which, together with the binding energies, can be used to characterize the samples. It was found that for samples which were not sufficiently homogen-

genized, nonconsistent values were obtained in the analysis of energy, intensity, and line asymmetry. The discrepancies could be removed by additional homogenization treatment of the samples.

### III. VALENCE-ELECTRON SPECTRA AND CORE-LINE ASYMMETRIES

Figure 1 shows core-level and valence-electron spectra for a few of the investigated alloys. There are several properties of these spectra which change systematically with the alloy concentration. First of all we note a chemical shift of the Pd and Cu core levels which amounts to about 1 eV. Both the Pd and the Cu core levels shift towards higher binding energies with increasing Cu concentration. A similar increase of binding energies was recently found for the Pd-Ag alloy system as a function of Ag concentration.<sup>19</sup> The high asymmetry of the Pd core-electron lines from pure palladium is considerably reduced in the spectra from the Cu-rich alloys while the Cu peaks retain their low asymmetries over the whole concentration range. Later on in this section we will correlate these observations with properties of the alloy valence band.

The behavior of the valence-band spectra is shown in greater detail in Fig. 2. Looking first at the spectra of the pure metals we note that these have partially overlapping *d* bands. The Pd *d* band extends over a region of 5 eV below the Fermi level. Copper has a narrower *d* band located between 2 and 5 eV from the Fermi level. We now want to understand the behavior of the valence bands of the alloys in terms of variations in the copper and palladium subbands.

Knowing the valence-band shapes of the pure metals, we can get a qualitative estimate of the sub-band shapes also for the *dilute* alloys. Apart from

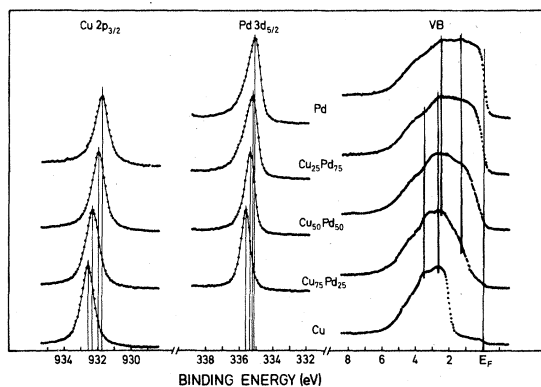


FIG. 1. Core- and valence-electron spectra for some  $\text{Cu}_x\text{Pd}_{1-x}$  alloys, including the pure constituents.

some small changes in the details of the partial density of states of the major component due to the destruction of the symmetry of the crystal, we expect it to be mainly the same as for the pure element. Most important is that we expect the width and the position of this partial density of states to be largely the same as that for the pure metal. Under these assumptions the subband of the minority component can be obtained by a simple subtraction procedure. The procedure we have used is to reduce the intensity of the valence band (for the pure metal) of the majority component according to the alloy concentration and then to subtract this from the measured alloy spectrum.<sup>22</sup> The so-obtained results for the alloys  $\text{Cu}_{93}\text{Pd}_{07}$  and  $\text{Cu}_{06}\text{Pd}_{94}$  are shown in Fig. 3. There we also include the results of our subtraction procedure for two somewhat more concentrated alloys.

For the copper-rich alloy the difference spectrum, i.e., our estimate of the Pd partial density of states, shows a pronounced peak at about 1.8 eV below the Fermi level. This result is in agreement with data from x-ray emission spectroscopy<sup>1</sup> and from a previous ESCA investigation by Hüfner *et al.*<sup>3</sup> A similar behavior for the silver-palladium and gold-palladium systems has also been found.<sup>3</sup> For the latter system the recent work by Nicolson *et al.*<sup>5</sup> confirms this finding. The only qualitative differ-

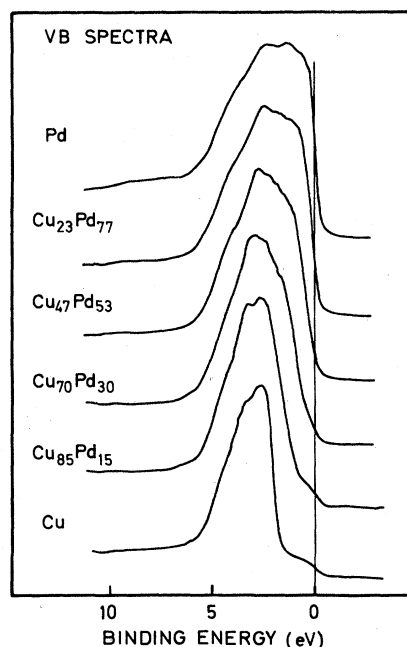


FIG. 2. Valence-electron spectra for a set of  $\text{Cu}_x\text{Pd}_{1-x}$  alloys, including pure Cu and Pd.

ence between our present copper-palladium system and the silver-palladium one<sup>3</sup> seems to be the tail tending towards the bottom of the valence band for the Cu-based alloy. The absence of this tail in the corresponding silver alloy<sup>3</sup> can be explained by the fact that silver has a more tightly bound *d* band than copper, and that there is only slight overlap in energy between the narrow Pd VBS (virtual bound state) and the silver *d* band. When the host *d* band is moved closer to the Pd VBS (as in copper) the bands start to overlap and the lower part of the VBS will get spread out over a wider energy range. From Fig. 3 we note that the smearing out of the Pd states starts at the energy onset of the copper *d* band. Also, the palladium-gold valence-band data<sup>3</sup> (where again the host *d* band is closer to the Pd VBS, but where the VBS is somewhat less bound than in copper) shows a tendency of the high-energy part of the Pd *d* states to become smeared out, but less so than that in copper. There remains, however, the question of whether the tail structure in Cu-Pd is a true feature of the Pd *d* band or just an artifact of the subtraction procedure. Support for the tail structure can be found from Pd  $L_{III}$  x-ray emission spectra<sup>1</sup> and coherent-potential-approximation-like calculations.<sup>24</sup> The tail would also suggest that the Pd *4d* states are more involved in bonding in the copper alloy than they are in the silver alloy. Therefore, the larger chemical shift of the Pd  $3d_{5/2}$  line in the copper host (0.8 eV) as compared to the silver host [0.5 eV (Ref. 19)] seems to support the reality of the tail structure. However, this argument requires that the Pd core-hole final-state effects are comparable for the Ag and Cu hosts.

Turning now to the palladium-rich alloys in Fig. 3 we find that the difference spectrum extends over almost the whole region of the Pd *d* band.<sup>25</sup> These results seem to imply that for low Cu concentrations the Cu *d* band hybridizes strongly with the host *d* band and more or less loses its identity. In fact, a similar result was observed for the Pd-Au system where the  $5d_{5/2}$  part of the Au *d* band could not be identified in the spectrum for high palladium concentrations.<sup>5</sup> On the other hand, the  $5d_{3/5}$  part, which does not overlap the Pd *d* band, was still found to be quite pronounced even at the lowest gold concentrations. These results and our present one for copper suggests that in transition-metal alloys with low concentration of coin metals, the coin metal subband will be quite strongly spread out in energy provided it has an energy overlap with the host *d* band.

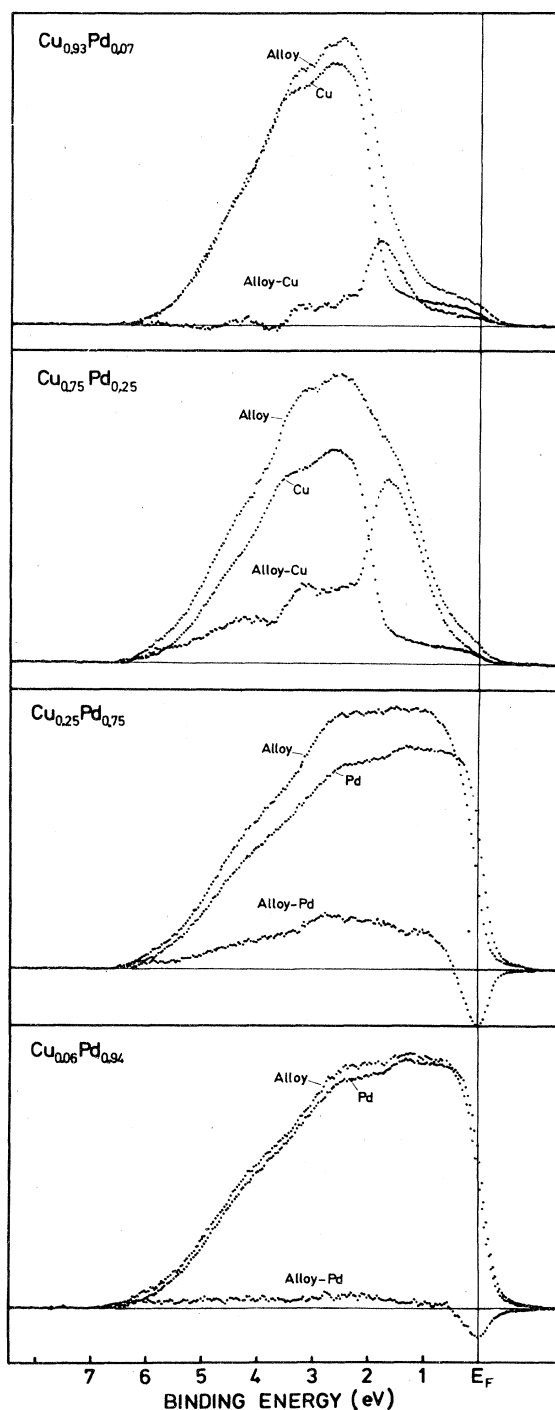


FIG. 3. Difference spectra for dilute copper palladium alloys, see Ref. 22.

Another feature seen in the palladium-rich alloys, Fig. 3, is the slight withdrawal of the Pd *d* band from the Fermi energy. This indicates an increased filling of the Pd *d* band when copper is brought into

palladium, which results in a lowering of the  $d$ -band density of states at the Fermi energy.

From Figs. 2 and 3 and the analogy with the Ag-Pd (Ref. 2) and Au-Pd (Refs. 3 and 5) systems we arrive at the following description for the behavior of the subbands. The two subbands are centered close to the positions of the bands of the pure metals. The filling of the region between the Cu  $d$  band and the Fermi level as the palladium concentration increases is thus an effect of the broadening of the Pd  $d$  subband. The density of states at the Fermi level [ $\rho(E_F)$ ] will then largely be determined by the Pd  $d$  subband. In Fig. 4 the intensity at the Fermi level  $I(E_F)$  as determined from the Cu-Pd spectra is plotted. The sharp rise in  $I(E_F)$  can be used to determine at what palladium concentration the Pd  $d$  band reaches the Fermi level. From Fig. 4 one can see that this occurs at a concentration close to 50 at. %. In general, we cannot expect that  $I(E_F)$  can be used as a direct measure of  $\rho(E_F)$ . This is due to the fact that  $I(E_F)$  might be strongly modulated by variations in the photoelectric cross section. However, in the case of the Cu-Pd alloys the rise in  $I(E_F)$  for higher palladium concentrations is almost entirely due to palladium  $d$  states, which is why we expect such modulation effects to be small.

Another measure of  $\rho(E_F)$  can be obtained from specific-heat data. Apart from a phonon enhancement factor the electronic contribution to the specific heat is expected to be proportional to  $\rho(E_F)$ . In Fig. 4 the specific heat for  $\text{Cu}_x\text{Pd}_{1-x}$  (Ref. 26) has

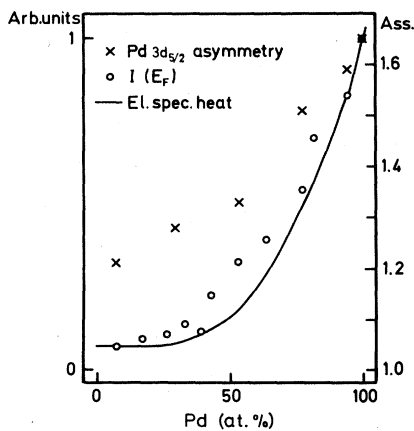


FIG. 4. Pd  $3d_{5/2}$  core-line asymmetry compared to two measures of the density of states at the Fermi level.  $I(E_F)$  denotes the photoelectron intensity at the Fermi level. The electronic specific heat is obtained from Ref. 26.

been plotted against the alloy concentration. As can be seen from the figure these two measures of  $\rho(E_F)$ , the electronic specific heat and  $I(E_F)$ , give almost identical results.

In Fig. 5 the measured Pd  $3d_{5/2}$  line asymmetry is plotted as a function of the alloy concentration. (The asymmetry ratio  $\Delta_1/\Delta_2$  is defined in the inset of Fig. 5.) From this it is clear that the Pd asymmetry is a strong function of the atomic composition. This asymmetry is also included in Fig. 4 and, as can be readily seen, it correlates quite well with the electronic specific heat and the photoelectron intensity  $I(E_F)$ . It has been demonstrated that the core-line asymmetry depends on the local density of states at the Fermi level.<sup>12</sup> Since  $\rho(E_F)$  for the  $\text{Cu}_x\text{Pd}_{1-x}$  alloy system is largely determined by the Pd density of states, the results in Fig. 4 are in conformity with the conclusions in Ref. 12. For low concentration of palladium the Pd  $3d_{5/2}$  asymmetry becomes comparable to that of the Ag  $3d_{5/2}$  line in pure silver. This seems rather reasonable in view of the almost total withdrawal of the Pd  $4d$  valence band from the Fermi level (see the difference spectrum for  $\text{Cu}_{93}\text{Pd}_{07}$  in Fig. 3). In comparison with palladium the Cu  $2p_{3/2}$  core-line asymmetry is much less dependent on the alloy concentration. This is again in line with the view that the asymmetry originates from the local density of states. The slightly larger Cu asymmetry for higher palladium concentrations might then be caused by an increase of the  $3d(\text{Cu})$ - $4d(\text{Pd})$  hybridization, which brings part of the local Cu  $3d$  density of states closer to the Fermi energy.

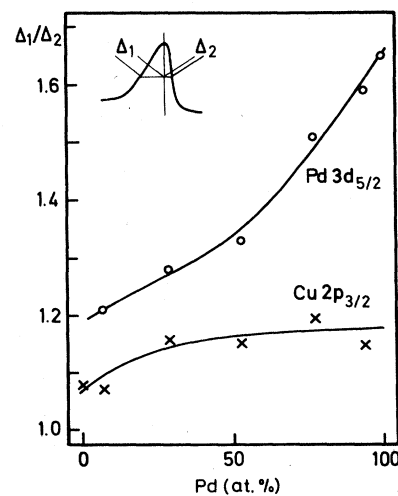


FIG. 5. Comparison of the Cu  $2p_{3/2}$  and Pd  $3d_{5/2}$  core-line asymmetries as a function of Pd concentration.

In connection with the valence-band spectra we would also like to discuss some features of the Pd  $M_{45}N_{45}N_{45}$  Auger spectrum. The general appearance of this spectrum is shown in the inset of Fig. 6. The main peak in the spectrum originates from the  $M_5N_{45}N_{45}$  process ending in the  $N_{45}N_{45}(^1G_4)$  final state.<sup>20</sup> For pure palladium this quasiatomic interpretation is strongly supported by the distinct displacement of about 3.6 eV between the pronounced features in the measured spectrum and the self-convoluted one.<sup>20</sup> The two-hole final state ( $N_{45}N_{45}$ ) of the Auger spectrum relative to the Fermi energy is obtained by relating the Auger kinetic energies to the binding energies of the  $M_4$  and  $M_5$  lines. An enlarged picture of the part of the Auger spectrum (indicated by the dotted arrow in the inset figure) which is close to the  $M_4$  line [ $E_F(3d_{3/2})$ ] is shown in Fig. 6 for some of the alloys. A vestige of a bandlike behavior can clearly be seen in these Auger spectra. (For a discussion of the relation between the quasiatomic and bandlike part of an Auger spectrum for narrow  $d$ -band materials, see Refs. 27 and 28.) Aside from a line broadening this bandlike part of the double  $d$ -hole final state starts at the Fermi level in pure palladium and the low-copper-concentration alloys. This is in agreement with the corresponding valence-band spectra (Fig. 3), where the Pd  $d$  band extends to the Fermi energy. For

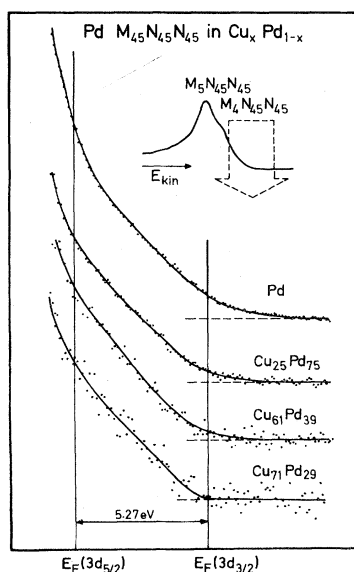


FIG. 6. Onset of the  $M_4N_{45}N_{45}$  Auger intensity is compared for a set of  $Cu_xPd_{1-x}$  alloys. This part of the spectrum is almost entirely bandlike. The withdrawal of the Pd local density of states from the Fermi level for lower Pd concentrations is demonstrated.

the copper-rich alloys (and especially clear for  $Cu_{71}Pd_{29}$ ) the onset of the bandlike transition is displaced from the Fermi level. This is again in agreement with the valence-band spectra since, as already commented on, for Pd concentrations of less than about 50 at. % the Pd  $d$  density of states no longer intersects the Fermi level. Unfortunately, the rather broad structures in the Auger spectra prevent a detailed determination of the intensity ratio between the quasiatomic and bandlike transitions.

#### IV. CHEMICAL SHIFTS

One of the most important properties of a photoelectron or an Auger spectrum is that the electron kinetic energies undergo displacements which depend on the chemical environment of the studied atom (chemical shifts).<sup>1,4,29-33</sup> Especially for molecular systems these chemical shifts have been found to be a most valuable tool for the study of the valence-electron structure. From highly developed quantum-chemical methods [such as  $\Delta$ SCF (self-consistent-field) and transition potential models<sup>34,35</sup>], where relaxation effects are taken into account, much has been learned about the influence of final-state effects on the chemical shifts. After proper considerations of these relaxation effects one still very often finds a direct relation between the shift and the formal charge of the atom. Furthermore, for molecular systems a first interpretation of the chemical shift can often be given in terms of the so-called group shifts.<sup>31</sup> Behind the group-shift idea lies the assumption that the shifts caused by groups attached to the same atom are independent of each other and that the total shift of the atom under study may be written as a sum of such partial shifts caused by each of its ligand groups. For metallic solids relatively little has been done concerning the fundamental understanding and interpretation of the chemical shifts and nothing comparable to the concept of group shift has been developed. One obvious complication is that these alloy shifts are quite small ( $\leq 1$  eV) in contrast to molecular systems where they often are as large as 5 eV. This holds true both in photoelectron and Auger electron spectroscopy. Therefore, the accuracy of any model which is meant to deal with alloy chemical shifts must be very high. Hence, models which treat the shifts as a balance between several relatively large terms will meet considerable difficulties.

One of the key problems to the description of the shifts in metallic systems is to account for the role of the metallic environment on the core-level binding energies and the Auger electron energies. Re-

cently a simple and accurate method for describing the binding-energy shift of a core electron in a free atom relative to the condensed atom in its metallic state was devised by Mårtensson and Johansson.<sup>13,14</sup> The basic assumption in their method is that of a completely screened final state of the core-ionized atom in the metal. Furthermore, it is assumed that the final-state valence-electron distribution can be substituted by that of an impurity atom with charge  $(Z + 1)$  in the original  $Z$ -atomic metal. The final state is then reached from the initial state by means of a Born-Haber cycle, in which the energy of solution for a  $(Z + 1)$  impurity ion (of charge  $+1$ ) in a metal host  $Z$ , gives a major contribution to the core-level shift. By this method, shifts between the metallic and the vapor phase have been obtained with high accuracy. It is straightforward to extend the treatment in order to describe the core-level shift of an atom  $A$  in its metallic state and if dissolved in a metallic matrix (which we will denote by  $B$ ). Thereby one arrives at the following relation for the shift  $\Delta E_c$  (Refs. 14 and 15):

$$\Delta E_c = E(A;B) + E(A+1;A) - E(A+1;B), \quad (4.1)$$

where  $E(A;B)$  is the energy of solution of a metallic atom  $A$  in the matrix  $B$ .  $A + 1$  is the  $(Z + 1)$  element relative to  $A$ . The first term can be looked upon as the change in the initial-state bonding properties of the component  $A$  in the matrix  $B$  relative to its bonding properties in its own host. The remaining two terms in Eq. (4.1) represent the change of the screened final-state conduction-electron metallic bonding in the host  $A$  relative to that in the matrix  $B$ . If  $B$  is a binary system  $AB$ , the last term in Eq. (4.1) involves a ternary system. However, in the case of a dilute system  $AB$ , with low concentration of the  $A$  component, all the terms in Eq. (4.1) reduce to a good approximation to solution energies of binary alloys. This will, of course, greatly simplify the analysis.

Recently this approach has been used to investigate chemical shifts for a large number of dilute alloys.<sup>14</sup> However, only in a few cases was it possible to perform the analysis in terms of experimental heat-of-solution data. Therefore the analysis was instead made by using Miedema's semiempirical scheme<sup>16-18</sup> for the heats of solution entering Eq. (4.1). Thereby a most encouraging agreement was obtained between these semiempirically calculated shifts and the experimental ones. Another recent application of Eq. (4.1) was made in Ref. 19 for the chemical shift of the  $\text{Pd } 3d_{5/2}$  line in  $\text{Pd}_x\text{Ag}_{1-x}$  al-

loys. In this case the  $A + 1$  element in relation (4.1) is nothing but the other alloy component  $B$ . Thus in this particular case only binary-alloy terms enter the relation for  $\Delta E_c$  and from this the heats of formation of the  $\text{Pd-Ag}$  alloy system can be extracted from the measured chemical shifts. The agreement with thermochemical experiments is very good.<sup>19</sup>

We will now discuss the chemical shifts for the  $\text{Cu}_x\text{Pd}_{1-x}$  alloy system in connection with Eq. (4.1). For this binary system we will meet the general problem of the ternary term. We will first concentrate on the chemical shifts of the photoelectrons and later discuss the Auger electron shifts. For  $\text{Cu}_x\text{Pd}_{1-x}$  alloys the first term in relation (4.1) is experimentally known.<sup>36,37</sup> It would therefore be possible to use the measured shifts together with Eq. (4.1) to extract heats of solution for  $\text{Zn}$  and  $\text{Ag}$  impurities in the  $\text{Cu}_x\text{Pd}_{1-x}$  alloys, since  $\text{Zn}$  and  $\text{Ag}$  are then the  $(Z + 1)$  elements of  $\text{Cu}$  and  $\text{Pd}$ , respectively.

In Fig. 7 we have plotted the measured  $\text{Pd } 3d_{5/2}$  and  $\text{Cu } 2p_{3/2}$  core-level shifts. For later discussion the experimental  $\text{Pd } M_5N_{45}N_{45}^1G_4$  and  $\text{Cu } L_3M_{45}M_{45}^1G_4$  Auger final-state shifts have also been included. For the present purpose of performing a detailed study of Eq. (4.1) for a binary system of a general type, it is not quite ideal to have palla-

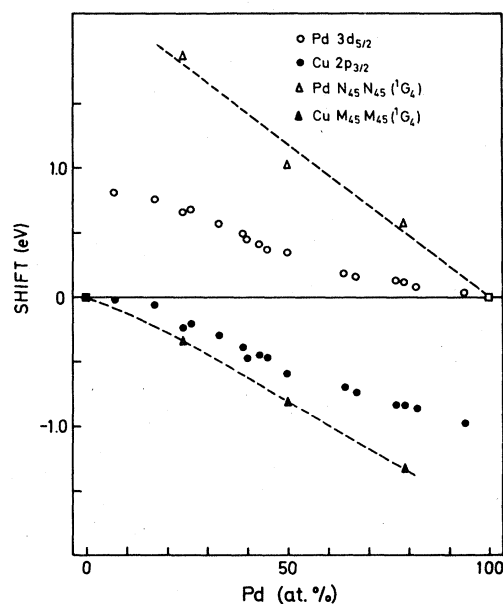


FIG. 7. Summary of measured single- and double-hole shifts. The lines drawn through the points which represent the double-hole states serve only as a guide for the eye.

dium as one of the alloy components, the reason being the pronounced asymmetry of its core lines (compare with the preceding section), which furthermore varies with the alloy concentration. Since the asymmetry leads to an apparent shift of the peak maximum to higher binding energies, a correction for this has to be made. The problems connected with the correction procedure have been extensively discussed in Ref. 38. In the present case line profiles obtained by convoluting the  $3d_{5/2}$  spectrum in the dilute palladium limit with the parametrized asymmetry function proposed by Mahan<sup>8</sup> were fitted to the  $3d_{5/2}$  spectra at higher palladium concentrations. The shift in the  $3d_{5/2}$  peak position when convoluted with the asymmetry function gives the correction to the chemical shift. The advantage of measuring these corrections relative to the  $3d_{5/2}$  spectrum in the dilute palladium limit is that the lifetime broadening and the spectrometer function are inherent in the procedure. Adding the correction in the dilute palladium limit, obtained by fitting a Doniach-Sunjić line profile<sup>7</sup> to the spectrum, we arrive at the result showed in Fig. 8. As can be seen, the corrections are quite substantial for the Pd-rich alloys, but decrease, as expected, with decreasing palladium concentration. In Fig. 7 the corrected chemical shifts are plotted. The corresponding correction for the Cu  $2p_{3/2}$  line is only of minor importance and no asymmetry corrections are needed for the chemical shifts. To obtain the final-state energy, relative to the Fermi energy, of the main peak of the  $M_5N_{45}N_{45}$  Auger spectrum, we have chosen to subtract the binding energy of the apparent peak position of the  $M_5$  line. This was also done in Fig. 6.

To facilitate the discussion of the Pd  $3d_{5/2}$  line shifts in the  $\text{Cu}_x\text{Pd}_{1-x}$  alloys we rewrite Eq. (4.1)

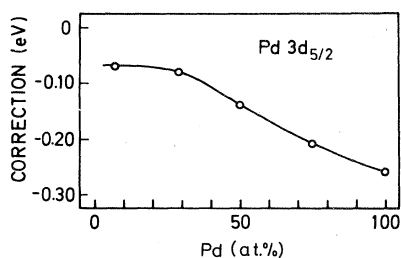


FIG. 8. Difference between the true and apparent Pd  $3d_{5/2}$  core-line positions as a function of palladium concentration. The procedure used to obtain these corrections is described in the text. Note also, in connection with Figs. 4 and 5, that this curve probably provides a more accurate measure of the variation in the core-line asymmetry than the previously used one.

explicitly for this case:

$$\Delta E_c^{\text{Pd}} = E(\text{Pd}; \text{Cu}_x\text{Pd}_{1-x}) + E(\text{Ag}; \text{Pd}) - E(\text{Ag}; \text{Cu}_x\text{Pd}_{1-x}). \quad (4.2)$$

As already mentioned, for our present alloy system, the first term is known from experimental thermochemical data.<sup>36,37</sup> This is also the case for the second term, which, furthermore, does not depend on the alloy concentration. The measured binding-energy shift of the Pd  $3d_{5/2}$  level amounts to about 0.8 eV for the copper-rich alloys. According to Eq. (4.2) the variation of this shift with concentration should now correspond to the variation of the difference between the heat of solution of a metallic Pd atom and a metallic Ag atom in the  $\text{Cu}_x\text{Pd}_{1-x}$  alloy. It is also clear from Eq. (4.2) that the extraction of thermochemical data from the core-level shifts might be a rather involved procedure. However, as in the present situation, when two of the terms are known, the third one can be derived. Since  $E(\text{Ag}; \text{Cu})$  and  $E(\text{Ag}; \text{Pd})$  both are known experimentally,<sup>36,37</sup> it seems possible here to estimate, with a reasonably accuracy, the third term  $E(\text{Ag}; \text{Cu}_x\text{Pd}_{1-x})$  for an arbitrary value of  $x$ , whereby we can make a direct comparison between the measured shift and a calculated one. The experimental value for  $E(\text{Ag}; \text{Cu})$  is  $-0.17$  eV and for  $E(\text{Ag}; \text{Pd})$  it is  $0.11$  eV. Therefore, to a first approximation, it seems reasonable to make a linear interpolation between the experimental extreme values for the intermediate concentrations. In Fig. 9 we compare the so-calculated chemical shifts with the

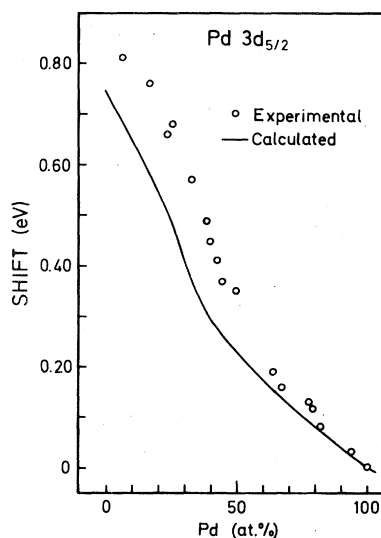


FIG. 9. Experimental and calculated Pd  $3d_{5/2}$  chemical shifts.



experimental data. As can be seen, the general agreement is good, the disagreement being of about a tenth of an eV in the low Pd concentration region. This discrepancy might originate from uncertainties in the employed thermochemical data and/or might be due to the ambiguities involved in the correction for the Pd  $3d_{5/2}$  asymmetry. Even so, the important conclusion is that the results in Fig. 9 certainly are most encouraging for further use of photoelectron line shifts for thermochemical investigations.

The Cu  $2p_{3/2}$  level shows a somewhat larger chemical shift than the Pd core levels. The binding energy varies from 932.57 eV for pure Cu to 931.60 eV for  $\text{Cu}_{0.6}\text{Pd}_{0.4}$ . For the Cu core-level shifts, Eq. (4.1) takes the form

$$\Delta E_c^{\text{Cu}} = E(\text{Cu}; \text{Cu}_x\text{Pd}_{1-x}) + E(\text{Zn}; \text{Cu}) - E(\text{Zn}; \text{Cu}_x\text{Pd}_{1-x}). \quad (4.3)$$

Thus the chemical shift involves the partial heat of solution of a Cu atom in  $\text{Cu}_x\text{Pd}_{1-x}$ , the impurity energy of a metallic Zn atom in pure copper, and finally, the heat of solution of zinc in  $\text{Cu}_x\text{Pd}_{1-x}$ . It turns out that the last entity will give a considerable contribution to the Cu core-level shift. Unfortunately, it is only in the limit of pure Cu that this energy is known experimentally, the value being  $E(\text{Zn}; \text{Cu}) = 0.24$  eV.<sup>36</sup> For the other limit, i.e., Zn in metallic Pd, we estimate the heat of solution from the Miedema scheme<sup>16-18</sup> and obtain  $E(\text{Zn}; \text{Pd}) = 1.49$  eV. This indicates that there is a considerable variation of the term  $E(\text{Zn}; \text{Cu}_x\text{Pd}_{1-x})$  as a function of alloy concentration. That this is reasonable is supported by the similar strong concentration dependence of the values for  $E(\text{Cd}; \text{Ag}_x\text{Pd}_{1-x})$  obtained by Steiner and Hüfner.<sup>19</sup> For this system, which is isoelectronic to ours, they furthermore found that  $E(\text{Cd}; \text{Ag}_x\text{Pd}_{1-x})$  varies almost linearly with concentration. This suggests that our term,  $E(\text{Zn}; \text{Cu}_x\text{Pd}_{1-x})$ , could be well approximated by a linear interpolation between  $x = 0$  and 1. From this we may now calculate the Cu  $2p_{3/2}$  shift in Eq. (4.3) and compare with experiment. This is done in Fig. 10. As can be seen, the experimental chemical shift is reproduced within 0.2 eV in this way. This is a satisfying agreement if we take into account that the large term  $E(\text{Zn}; \text{Pd})$  is not experimentally known.

To illustrate how the chemical-shift data can be used, we present the results for the Cu  $2p_{3/2}$  shifts in a different way. As already mentioned for the present alloys the first two terms in Eq. (4.3) are known from independent experiments. Therefore,

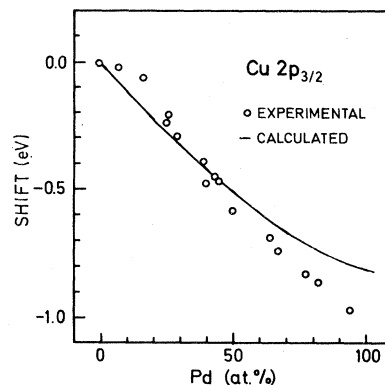


FIG. 10. Experimental and calculated Cu  $2p_{3/2}$  chemical shifts.

we can derive the third term from the chemical-shift data. The result from such an analysis is shown in Fig. 11. We have also included in the figure the two binary heat-of-solution energies as obtained from Miedema's theory.

We now turn to the analysis of the chemical shifts of the Auger electron lines. We will investigate these shifts in terms of the shifts of the Auger final-state energies (measured relative to the Fermi level). The Auger final-state energy is the energy required to create two core holes on the same atom. For the chemical shifts of these excitation energies we can derive an expression similar to the one in Eq. (4.1), but where we now have to invoke the  $(Z + 2)$  approximation. We obtain for the chemical shift of the double-hole state  $\Delta E_{cc}$  the following expression:

$$\Delta E_{cc} = E(A; B) + E(A + 2; A) - E(A + 2; B), \quad (4.4)$$

where  $A + 2$  is the  $(Z + 2)$  element relative to  $A$ .

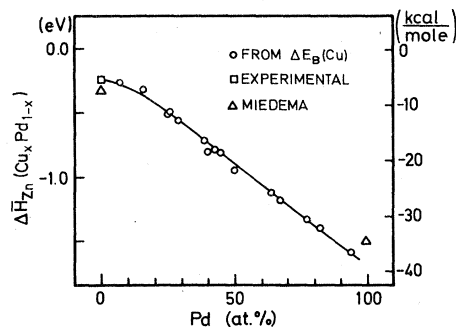


FIG. 11. Heat of solution of a Zn atom in  $\text{Cu}_x\text{Pd}_{1-x}$  alloys as obtained from the Cu  $2p_{3/2}$  chemical shift. The experimental value for Zn in Cu is taken from Refs. 36 and 37. For comparison, the binary values calculated according to Miedema (Refs. 16-18) are also included.

Otherwise, the terms in Eq. (4.4) have the same meaning as before.

We start by treating the Pd  $N_{45}N_{45}$  energy shifts. Note that here we regard the main peak of this final state as a localized  $d^8(^1G_4)$  configuration. In this case Eq. (4.4) takes the form

$$\Delta E_{cc}^{\text{Pd}} = E(\text{Pd}; \text{Cu}_x\text{Pd}_{1-x}) + E(\text{Cd}; \text{Pd}) - E(\text{Cd}; \text{Cu}_x\text{Pd}_{1-x}). \quad (4.5)$$

In this expression only the first term is known from independent experiments. For the last two terms we use Miedema's theory for  $E(\text{Cd}; \text{Pd})$  and  $E(\text{Cd}; \text{Cu})$  and make a linear interpolation for the general term  $E(\text{Cd}; \text{Cu}_x\text{Pd}_{1-x})$ . Thereby we obtain the results shown in Fig. 12. In view of the uncertainties in the thermochemical values the agreement with experiment is certainly acceptable. In Fig. 13 we have used the data in a different way and derived the energy for the term  $[E(\text{Cd}; \text{Cu}_x\text{Pd}_{1-x}) - E(\text{Cd}; \text{Pd})]$  by using the experimental final-state Auger shift and our expression (4.5). The behavior of this ternary-solution energy is quite similar to the corresponding term for a Cd impurity in the  $\text{Ag}_x\text{Pd}_{1-x}$  alloy as obtained from the Ag single-hole shift in Ref. 19, both as regards the magnitude and the linear dependence in concentration. Also, it is similar to our just previously obtained behavior of  $E(\text{Zn}; \text{Cu}_x\text{Pd}_{1-x})$ .

The expression for the Cu  $M_{45}M_{45}(^1G_4)$  two-hole chemical shift (as in Pd the two holes are regarded as localized) takes the following form:

$$\Delta E_{cc}^{\text{Cu}} = E(\text{Cu}; \text{Cu}_x\text{Pd}_{1-x}) + E(\text{Ga}; \text{Cu}) - E(\text{Ga}; \text{Cu}_x\text{Pd}_{1-x}). \quad (4.6)$$

Again the first term is known from thermochemical data. In this case we content ourselves with deriv-

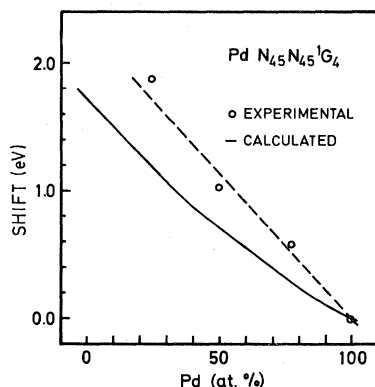


FIG. 12. Experimental and calculated double-hole shifts for Pd.

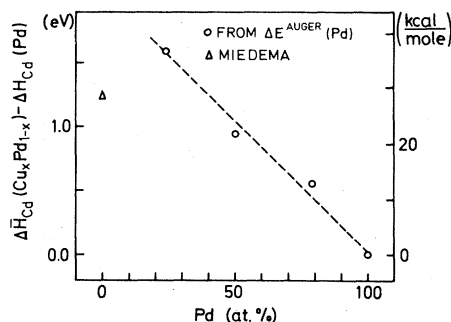


FIG. 13. Heat of solution of a Cd atom in  $\text{Cu}_x\text{Pd}_{1-x}$  alloys, relative to the heat of solution in pure Pd, as obtained from the Pd Auger final-state shifts.

ing the quantity  $E(\text{Ga}; \text{Cu}_x\text{Pd}_{1-x}) - E(\text{Ga}; \text{Cu})$  from the Auger final-state chemical shifts and the above relation. The results are shown in Fig. 14 where also the Miedema semiempirical value is included.

It is of particular interest to study the difference  $\delta E$  between the one-hole and two-hole shifts (i.e., the Auger electron shift). From relations (4.1) and (4.4) we obtain

$$\begin{aligned} \delta E &= \Delta E_c - \Delta E_{cc} \\ &= E(A + 1; A) - E(A + 1; B) \\ &\quad - E(A + 2; A) + E(A + 2; B). \end{aligned} \quad (4.7)$$

Thus for this difference only final-state terms enter. In Fig. 15 we have plotted this difference for Cu as well as for Pd for our present alloys. For both elements the difference  $\delta E$  shows a quite strong dependence on the alloy concentration. This very clearly demonstrates that the final-state relaxations depend on the chemical environment. This dependency has very often been neglected in discussion of chemical shifts.

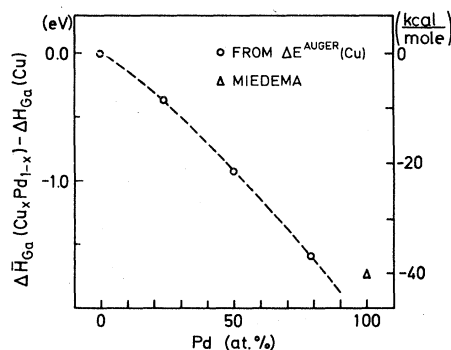


FIG. 14. Heat of solution of a Ga atom in  $\text{Cu}_x\text{Pd}_{1-x}$  alloys, relative to the heat of solution in pure Cu, as obtained from the Cu Auger final-state shifts.

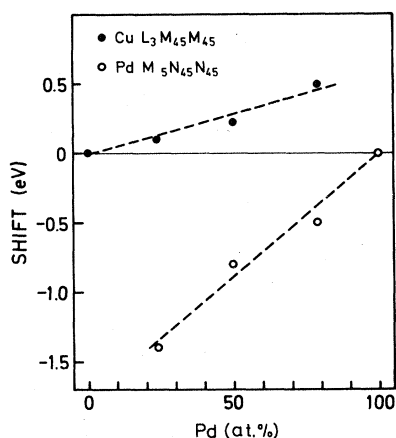


FIG. 15. Cu and Pd Auger electron shifts.

Finally, in this section we would like to demonstrate another possible use of the measured chemical shifts of the two components in a binary alloy, namely to derive the heat of formation of the studied alloy. For our present copper-palladium system this application is, however, not quite straightforward at this moment, since some of the contributing terms have to be approximated due to the present lack of certain thermochemical data. Nevertheless, we give the following analysis as a further demonstration of how measured chemical shifts might be utilized for extraction of thermochemical information. From Eqs. (4.2) and (4.3) we write the difference  $D(x)$  between the chemical shifts of Pd  $3d_{5/2}$  and Cu  $2p_{3/2}$  as

$$\begin{aligned} D(x) &= \Delta E_c^{\text{Pd}}(x) - \Delta E_c^{\text{Cu}}(x) \\ &= E(\text{Pd}; \text{Cu}_x\text{Pd}_{1-x}) - E(\text{Cu}; \text{Cu}_x\text{Pd}_{1-x}) \\ &\quad + E(\text{Ag}; \text{Pd}) - E(\text{Ag}; \text{Cu}_x\text{Pd}_{1-x}) \\ &\quad - [E(\text{Zn}; \text{Cu}) - E(\text{Zn}; \text{Cu}_x\text{Pd}_{1-x})]. \end{aligned} \quad (4.8)$$

This we rewrite as

$$\begin{aligned} D(x) &= E(\text{Pd}; \text{Cu}_x\text{Pd}_{1-x}) - E(\text{Cu}; \text{Cu}_x\text{Pd}_{1-x}) \\ &\quad + F_{\text{Ag}}(x) - F_{\text{Zn}}(x), \end{aligned} \quad (4.9)$$

where we have introduced two functions  $F_{\text{Ag}}(x)$  and  $F_{\text{Zn}}(x)$  defined as

$$\begin{aligned} F_{\text{Ag}}(x) &= E(\text{Ag}; \text{Pd}) - E(\text{Ag}; \text{Cu}_x\text{Pd}_{1-x}), \\ F_{\text{Zn}}(x) &= E(\text{Zn}; \text{Cu}) - E(\text{Zn}; \text{Cu}_x\text{Pd}_{1-x}). \end{aligned} \quad (4.10)$$

From these equations the heat of formation  $-\Delta H(\text{Cu}_x\text{Pd}_{1-x})$  can be obtained by use of the relation<sup>19,39</sup>

$$\begin{aligned} \frac{d}{dx}[-\Delta H(\text{Cu}_x\text{Pd}_{1-x})] &= E(\text{Cu}; \text{Cu}_x\text{Pd}_{1-x}) \\ &\quad - E(\text{Pd}; \text{Cu}_x\text{Pd}_{1-x}). \end{aligned} \quad (4.11)$$

From Eq. (4.9) this might be written as

$$\begin{aligned} \frac{d}{dx}[-\Delta H(\text{Cu}_x\text{Pd}_{1-x})] \\ = -D(x) + F_{\text{Ag}}(x) - F_{\text{Zn}}(x), \end{aligned} \quad (4.12)$$

and therefore we arrive at the following expression for the heat of formation:

$$\begin{aligned} -\Delta H(\text{Cu}_x\text{Pd}_{1-x}) &= \int_0^x [-D(x') + F_{\text{Ag}}(x') \\ &\quad - F_{\text{Zn}}(x')] dx'. \end{aligned} \quad (4.13)$$

For the present investigation the problem is that we do not know the functions  $F_{\text{Ag}}(x)$  and  $F_{\text{Zn}}(x)$ . However, for simplicity, we will now assume that they can be reasonably well approximated by linear expressions. Thus we write

$$F_{\text{Ag}}(x) \simeq [E(\text{Ag}; \text{Pd}) - E(\text{Ag}; \text{Cu})]x, \quad (4.14)$$

$$F_{\text{Zn}}(x) \simeq [E(\text{Zn}; \text{Cu}) - E(\text{Zn}; \text{Pd})](1-x).$$

The experimental values for  $E(\text{Ag}; \text{Pd})$ ,  $E(\text{Ag}; \text{Cu})$ , and  $E(\text{Zn}; \text{Cu})$  are 0.11, -0.17, and 0.24 eV, respectively.<sup>36</sup> The experimental value for  $E(\text{Zn}; \text{Pd})$  is not known for the moment. However, below we will use the boundary condition  $-\Delta H(\text{Cu}_x\text{Pd}_{1-x}) \rightarrow 0$ ,  $x \rightarrow 1$  in order to determine  $E(\text{Zn}; \text{Pd})$ . From the experimental shifts we find that the function  $D(x)$  can be quite well approximated by  $(0.99-0.18x)$  eV. From Eq. (4.13) and the boundary condition we then find  $E(\text{Zn}; \text{Pd}) = 1.76$  eV. From this it is now very simple to calculate the heat of formation  $-\Delta H(\text{Cu}_x\text{Pd}_{1-x})$  from our measured chemical shifts. We find

$$-\Delta H(\text{Cu}_x\text{Pd}_{1-x}) = 0.53x(1-x) \quad (4.15)$$

(in units of eV). In Fig. 16 we compare this expression with the experimental values of the heat of formation. Remembering the approximations we have made for the functions  $F_{\text{Ag}}$  and  $F_{\text{Zn}}$ , the agreement is quite good. The experimental curve shows a slight asymmetry around the line  $x = 0.5$  which is absent in our calculated curve. In the upper part of Fig. 16 we compare the partial heats of formation of Cu and Pd, respectively, in the  $\text{Cu}_x\text{Pd}_{1-x}$  alloy. Again the agreement with experiment is quite

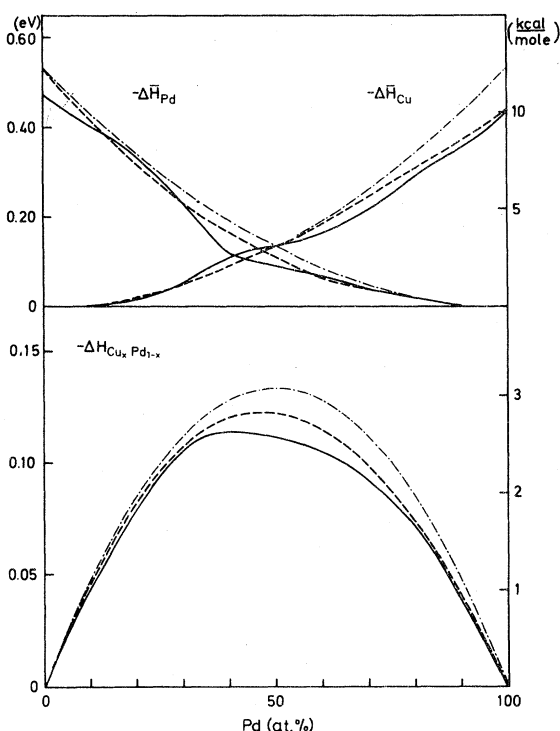


FIG. 16. Heat-of-formation curves for the  $\text{Cu}_x\text{Pd}_{1-x}$  alloy system derived from chemical-shift measurements. Both a linear approximation (dash-dotted line) and a quadratic approximation (dashed line) has been used for the  $\text{Cu } 2p_{3/2}\text{-Pd } 3d_{5/2}$  relative shift. The full lines represent the calorimetric data from Ref. 37.

reasonable. As we have mentioned earlier, in the isoelectronic alloy  $\text{Ag}_x\text{Pd}_{1-x}$  Steiner and Hufner<sup>19</sup> found that the quantity  $F_{\text{Cd}}(x)$  corresponding to our present  $F_{\text{Zn}}(x)$ , behaves linearly with concentration. Thus our second approximation in Eq. (4.14) is expected to be good. For the quantity  $E(\text{Ag};\text{Cu}_x\text{Pd}_{1-x})$  it seems reasonable to assume that it behaves in a similar way as  $E(\text{Cu};\text{Cu}_x\text{Pd}_{1-x})$ . In the upper part of Fig. 16 we notice that this quantity is better represented by a quadratic function than by a linear one. Therefore it might be more reasonable to make the following approximation for  $F_{\text{Ag}}(x)$ :

$$F_{\text{Ag}}(x) = [E(\text{Ag};\text{Pd}) - E(\text{Ag};\text{Cu})] \times [1 - (1-x)^2]. \quad (4.16)$$

Substituting this into Eq. (4.13) we obtain  $E(\text{Zn};\text{Pd}) = 1.67$  eV. This is in reasonable agreement with the Miedema value 1.49 eV. The expression for the heat of formation takes the form

$$-\Delta H(\text{Cu}_x\text{Pd}_{1-x}) = 0.44x - 0.35x^2 - 0.09x^3. \quad (4.17)$$

This function is also plotted in Fig. 16 and a slightly improved agreement with experiment can be seen. Moreover, this expression is somewhat asymmetric. In the upper part of Fig. 16 it can be seen that the corresponding partial heats of formation agree relatively well with experiment and that the direction of the asymmetry is correctly accounted for. It should also be noted that the use of a quadratic form for  $F_{\text{Ag}}(x)$  does not greatly modify the magnitude of  $-\Delta H(x)$ .

## V. DISCUSSION

In the present work we have studied the valence-band-electron spectrum for a number of  $\text{Cu}_x\text{Pd}_{1-x}$  alloys by means of ESCA. To obtain the density of states of the low-concentration component a subtraction procedure was applied. The obtained results are in good overall agreement with other studies of related binary alloy systems (for example, Pd-Au and Pd-Ag). We have also studied the core-level asymmetries and shown that there is a good correlation between the local density of states and the degree of asymmetry. From the valence-electron spectra we found that the measured intensity at the Fermi level scales well with the density of states at the Fermi surface  $\rho(E_F)$  as obtained from specific-heat measurements. From our study of the  $\text{Pd } M_{45}N_{45}N_{45}$  Auger spectrum we could also identify a contribution from a bandlike final state in addition to the dominating quasiautomatic part of the spectrum.

The main aspect of this work was, however, to study the chemical shifts of the  $\text{Pd } 3d_{5/2}$  and  $\text{Cu } 2p_{3/2}$  core-level lines as a function of the alloy concentration. Earlier studies for a number of various dilute systems have indicated that chemical shifts might become a useful technique for thermochemical investigations. These dilute systems were carefully chosen so that only binary alloy systems entered the expression for the chemical shift. Here we have studied an alloy system of a more general type, where the full complexity of the chemical shift enters. Of course this renders the analysis much more difficult, but serves as an example of what type of information can be derived from the chemical shifts in a more general case. Furthermore, this example illustrates what kind of terms have to be included in a full microscopic treatment of the shifts.

The basic idea, which permits a thermochemical interpretation of the shifts, is the assumption of a complete screening of the core-ionized site. This screening is provided by a redistribution of the

valence-band electrons. In the presence of a core hole the screening valence-electron density distribution around the ionized site will then be very similar to that for a  $(Z + 1)$ -impurity atom in a  $Z$ -metal host or, more generally, in a  $Z_x Y_{1-x}$  metallic alloy host. In the present case, where the chemical shift is defined relative to the pure metal, the  $(Z + 1)$  approximation enters in a differential way. The fact that the  $(Z + 1)$  approximation in itself is very good then means that the  $(Z + 1)$  substitution will become very accurate when introduced in connection with chemical shifts.

A more severe approximation that enters the thermochemical interpretation of the shift [see Eq. (4.1)] is the fact that the photoionization is a vertical process, while the thermochemical approach presupposes a thermal ionization process. However, since in general the atomic volume of the  $(Z + 1)$  and  $Z$  elements do not differ very much, this should not be a too restrictive limitation of the method. In the final state of an Auger process, where a  $(Z + 2)$  substitution is made in the thermochemical explanation of the shift, the difference between the vertical and thermal ionization energies might become somewhat more pronounced. In a microscopic theoretical calculation the vertical process is, of course, much more easily treated than the corresponding thermal process, where the uttermost difficult problem of the nuclei displacement has to be considered. Therefore, if for some very well characterized system one could isolate a definite difference between the vertical and thermal ionization energy, that piece of in-

formation could be most valuable in the theory of alloys, since one could thereby, to a first approximation, separate the electronic and the nuclei relaxation energies from each other.

The main conclusion of this work is that accurate measurements of chemical shifts give promise of becoming a very useful means for rapid determinations of thermochemical data. Thereby it should be noted that the relative changes of the core-level binding energies can be determined with a considerably higher accuracy than the absolute value for the binding energy. This in turn means that for well-characterized and favorable systems the accuracy of the electron spectroscopy data, for quantities such as the heat of formation, can be quite comparable with that of thermochemical measurements. We believe we have here verified this for the  $\text{Cu}_x\text{Pd}_{1-x}$  alloy system in this paper. For this particular case, however, the interpretation of the data is made somewhat more difficult, due to the asymmetry of the  $\text{Pd } 3d_{5/2}$  line. As a final remark we would like to stress once more that ESCA *calorimetry* might become a useful and rapid technique for thermochemical investigations in the realm of material science.

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