Compton profile of palladium

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In this paper we present the results of a Compton-profile study on polycrystalline palladium. The measurements have been made by scattering 59.54-keV photons. Theoretical Compton profiles have been calculated with use of the renormalized-free-atom (RFA) model and the augmented-plane-wave method. Best agreement between the measured and calculated values was found for the $4d^{9.7}5s^{0.3}$ configuration within the RFA model.

I. INTRODUCTION

Palladium is a particularly interesting transition metal because of its unusual properties.[1] It is also known as compensated metal because outside the inner shells there are ten electrons which must be shared by the *s* and *d* bands in the metal. In the mid 1960s, Vuillemin and Priestley[2] studied the Fermi surface in Pd using the de Haas–van Alphen (dHvA) method and found that the *s* bands contained 0.36 ± 0.1 *e*/at., which implied an equal number of holes in the *d* band, a result also consistent with the galvanomagnetic data of Alekseevskii *et al.*[3] Thereafter a number of theoretical calculations of the band structure using the augmented-plane-wave (APW) and other methods have been reported[4] and their predictions were subjected to experimental verification.[5–7]

In recent years there has been a renewed interest in the use of Compton scattering for probing the behavior of slowly moving valence electrons in solids.[8,9] The main reason for this is the fact that the Compton profile provides a direct test for the electron wave-function calculations and thereby for the electron structure. In our endeavor to extend the Compton scattering method to 4*d* metals, we studied Nb (Ref. 10) and Ag (Ref. 11). Here we investigate the case of polycrystalline Pd. It is worthwhile to mention that Lässer and Lengeler[12] had already applied this technique to study the state of hydrogen in PdH and, accordingly, they confined their effort to the difference profile for Pd and $PdH_{0.72}$. Theoretical electron momentum densities along the three principal directions and band profiles were first reported for Pd by Kanhere and Singru,[13] using the Hubbard approximation scheme, and by Podloucky *et al.*[7] thereafter, which were in good agreement with their measurement using 320 keV γ rays. In a later work, Hermalkar *et al.*[14] computed electron momentum densities for Pd and PdH employing the APW method and observed that their computed difference results generally agreed with the experiment of Lässer and Lengeler.[12] Recently we had reported preliminary results of our Compton profile study on polycrystalline Pd.[15] In this work, we present an accurate experimental Compton profile for valence electrons in Pd and compare it with theoretical results obtained from the renormalized-free-atom (RFA) model and the APW method. In Sec. II we describe the details of the measurement, and in Sec. III the calculation. In Sec. IV the results are presented and discussed in the light of these calculations. The conclusions are given in Sec. V.

II. EXPERIMENT

The experimental setup used in this investigation is shown in Fig. 1. It is similar to the one designed by Manninen and Paakkari[16] and is particularly suitable for measurements on polycrystalline samples. 59.54-keV γ rays from a 5-Ci annular ^{241}Am isotope were scattered by a foil of polycrystalline palladium having 0.13 mm thickness (99.99%). The sample was held vertically in a vacuum chamber, and the radiation scattered through a mean angle of 159° was detected by a planar Ge detector. The source-sample and sample-detector distances were 75 and 200 mm, respectively. The channel width was about 60 eV ($\sim$0.1 a.u.) and the total resolution of the Compton spectrometer was about 0.55 a.u. of momentum. About 100 000 counts/channel were collected at the Compton peak in three days time.

To correct for the background contribution, a separate measurement without any sample was taken and subtracted from the measured spectrum point by point after being properly scaled to the sample measurement time. The peak to background ratio was about 90:1. The intensity of the elastic peak was about twice that of the Compton peak. This contributed to small escape peaks around the center of the Compton peak. Their effect in the measured Compton spectrum was minimized by running the system with a weak ^{241}Am source in subtract mode until

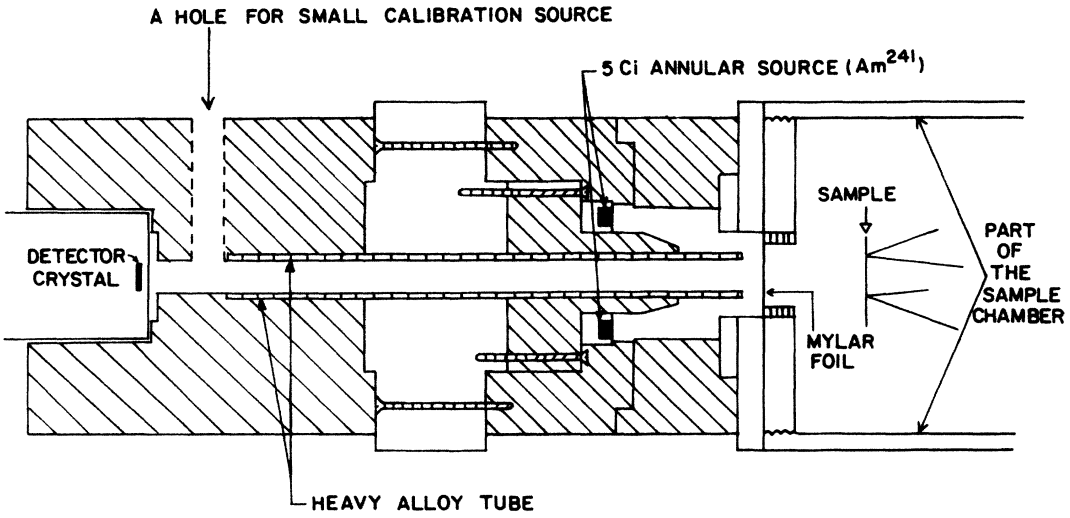

FIG. 1. Schematic diagram of the source-collimator assembly.

the elastic peak almost disappeared from the raw data.[10] The profile was then corrected for instrumental resolution effects, sample absorption, and energy dependence of the Compton-scattering cross section. Finally, the profile was converted to the momentum scale to obtain $J(q)$ and normalized to 18.321 electrons, being the area of the free-atom Compton profile excluding the contribution of $1s^2$ electrons, which do not contribute due to their large binding energy.[17]

A correction for multiple Compton scattering is essential if one is interested in accurate Compton profiles. Therefore, a Monte Carlo procedure which removes the contribution of elastic and inelastic double scattering events was applied following the method of Halonen *et al.*[18] The ratio of double to single scattering turned out to be about 3.5% and the effect of this correction was about 1.4% at $J(0)$. This once again points out to the value of this correction.

III. CALCULATION

Since the theory of Compton scattering is well established,[8,9] we skip details and give only the key relation here. For a polycrystalline sample, the Compton profile $J(p_z)$ is given as

$$J(p_z)=\int_{p_z}^{\infty} p\langle\rho(\mathbf{p})\rangle\ , \tag{1}$$

where $\langle\rho(\mathbf{p})\rangle$ is the spherical average of the electron momentum density $\rho(\mathbf{p})$, p_z is the projection of the momentum $\mathbf{p}$ along the scattering vector and the integration is taken over the plane $p_z=$const. For the inner-core electrons it is sufficient to use free-atom wave functions, and their Compton profiles are available in the literature.[19] For band electrons, however, this is inadequate. Accordingly, we have followed two approaches developed by Berggren[20] and Hermalkar *et al.*[14]

In Berggren's approach based on the RFA model, free-atom Hartree-Fock wave functions are truncated at the Wigner-Seitz sphere and renormalized to one within the sphere to retain charge neutrality. Using the RFA wave functions, the Compton profile for $5s$ electrons was computed from the relation (Ref. 8)

$$J_{5s}(p_z)=4\pi\sum_{n=0}^{\infty}|\psi_0^c(K_n)|^2 G_n(p_z)\ , \tag{2}$$

where $\psi_0^c(K_n)$ is the Fourier transform of the RFA wave function. K_n is the nth reciprocal lattice vector, and $G_n(p_z)$ is an auxiliary function involving p_F, K_n, etc. The effect of truncation was very large for the $5s$ electrons because for Pd only 32% of the free-atom wave function was contained within the Wigner-Seitz sphere. For $4d$ electrons the corresponding value was 96%. From the RFA wave function shown in Fig. 2, as discussed earlier,[8,10,11] the Compton profile $J_{5s}(p_z)$ was calculated for a number of $4d$-$5s$ electron configurations from Eq. (2). For $4d^9 5s^1$ and $4d^8 5s^2$ configurations, free-atom Hartree-Fock wave functions were taken from the tables of Clementi and Roetti.[21] For the cases where the number of $5s$ electrons was up to 1.5, the wave function for $4d^9 5s^1$ was taken; but in the other cases the wave function for $4d^8 5s^2$ was considered. The value of p_F and normalization of $J_{5s}(p_z)$ were, however, according to the number of $5s$ electrons. In all, 15 of the shortest (K_n) vectors were considered in Eq. (2). For $4d$ electrons, the Compton profile was taken directly from the tables of Biggs *et al.*,[19] and after suitable multiplication were added to the $5s$ profiles.

The APW calculation was carried out following the procedure described in Ref. 14. The one-electron muffin-tin crystal potential was calculated from Lowdin's α-expansion technique by superposing atomic charge densities and Coulomb potentials up to 14 nearest neighbors. The atomic configuration chosen was $4d^{10}5s^0$ and full Slater exchange ($\alpha=1$) was taken. The energy eigen-

TABLE I. Compton profile $J(p_z)$ for valence electrons in polycrystalline Pd. The area under each profile is equal to 4.8329 electrons, being the area of the Compton profile of $4d^{10}$ electrons in the free atom in the momentum region 0–4 a.u. The experimental results are from this work and the values are obtained by subtracting the core contribution from the total profiles. Errors shown for some points in fact correspond to the total profile and hence represent their upper limit. Theoretical values are unconvoluted. The RIF is given for some points.

p_z (a.u.)	RFA $4d^{7}5s^{1}$ (e/a.u.)	RFA $4d^{9.7}5s^{0.3}$ (e/a.u.)	Free atom $4d^{10}$ (e/a.u.)	APW (e/a.u.)	Experiment after DS (e/a.u.)	RIF
0.0	3.454	3.132	2.822	3.233	3.034±0.041	0.2009
0.1	3.435	3.111	2.822	3.212	3.009	0.1861
0.2	3.377	3.058	2.822	3.149	2.987	0.0931
0.3	3.273	2.951	2.812	3.044	2.946	0.0391
0.4	3.131	2.810	2.802	2.896	2.852	−0.0035
0.5	2.936	2.708	2.776	2.726	2.725	−0.0278
0.6	2.680	2.657	2.720	2.581	2.627	−0.0327
0.7	2.439	2.575	2.634	2.479	2.523	−0.0261
0.8	2.340	2.469	2.528	2.381	2.364	−0.0026
1.0	2.094	2.205	2.256	2.168	2.092±0.036	0.0107
1.2	1.819	1.914	1.954	1.917	1.795	0.0086
1.4	1.523	1.603	1.638	1.603	1.565	−0.0019
1.6	1.255	1.321	1.352	1.286	1.337	−0.0046
1.8	1.012	1.066	1.092	1.017	1.158	−0.0006
2.0	0.802	0.850	0.872	0.827	0.968±0.026	0.0019
3.0	0.215	0.233	0.239	0.246	0.249	0
4.0	0.046	0.057	0.058	0.064	0.047	0

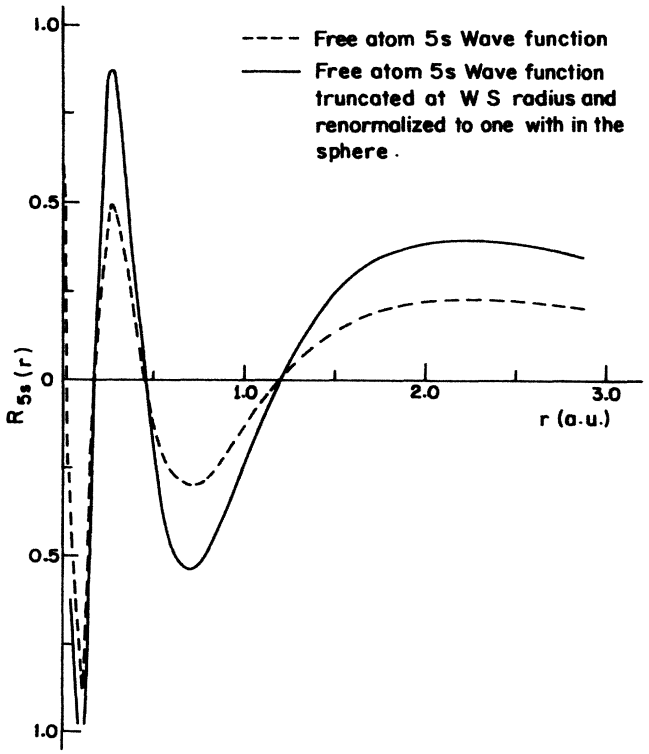

FIG. 2. The free-atom 5s wave function in Pd before (dashed line) and after (solid line) truncation and renormalization to one within the Wigner-Seitz sphere.

values and the corresponding eigenvectors were calculated at 89 **k** points in the $\frac{1}{48}$th Brillouin zone. The resulting band structure was found to be in good agreement with that of Mueller *et al.*[4] (Table I of Ref. 14). A set of 89 G vectors was included in the calculation giving $\rho_j(\mathbf{p})$ at about 250 000 points in the momentum space. The electron momentum density $\rho(\mathbf{p})$ was obtained for three symmetry directions by summing the contributions of all occupied bands. The spherical average $\langle\rho(\mathbf{p})\rangle$ as discussed in Eq. (1) was computed using the standard averaging formula:

$$\langle\rho(\mathbf{p})\rangle=\tfrac{1}{35}(10\rho_{100}+16\rho_{110}+9\rho_{111})\,. \tag{3}$$

Then the Compton profile for band electrons was determined from Eq. (1). All theoretical values, RFA and APW, were normalized to an area of 4.833 electrons corresponding to the area of the free-atom $4d^{10}$ Compton profile from 0 to 4 a.u.

IV. RESULTS AND DISCUSSION

The total experimental Compton profile for polycrystalline Pd after applying the various correction (Sec. II) is presented in Fig. 3. Errors for some points are also shown. Also presented here are the theoretical results convoluted with RIF,[22] from our RFA calculation for two configurations, namely, $4d^{9}5s^{1}$ and $4d^{9.7}5s^{0.3}$. The free-atom model with the $4d^{10}5s^{0}$ configuration[19] is also shown. In order to obtain the total $J(p_z)$, contributions from all inner electrons, except 1s, were taken from Ref. 19 and added to the valence-electron profiles. The solid

line is the total core contribution. In our experiment, 1s electrons were not excited because the recoil energy was less than their binding energy.[17] They, however, contribute via double scattering (elastic process), and for this we have applied suitable correction as discussed in Sec. II.

It is noteworthy that between 4 and 7 a.u. theory and experiment are very close and nearly follow the solid line, which simply represents the core contribution. In fact the differences between theory and experiment were less than 0.05 e/a.u. This can be understood from the fact that in the high-momentum region the contribution of band electrons almost vanishes and thus only the inner-electron contribution remains. Since these electrons are virtually unaffected on solid formation, the free-atom model gives a satisfactory explanation of the Compton profile in this region. In the different theoretical results, the same core has been considered and hence all these values are almost same. In the low-momentum region there are, however, significant differences. The free-atom values are smaller than the experimental values up to 0.5 a.u., but between 0.5 and 1.5 a.u. they become higher. The RFA values for $4d^9 5s^1$ case are higher initially but become lower after 0.8 a.u. The agreement was very poor for the $4d^8 5s^2$ configuration and thus they are not presented here. When 0.3 electrons were assigned to the 5s band ($4d^{9.7} 5s^{0.3}$) theory and experiment were in very good agreement in the entire momentum range.

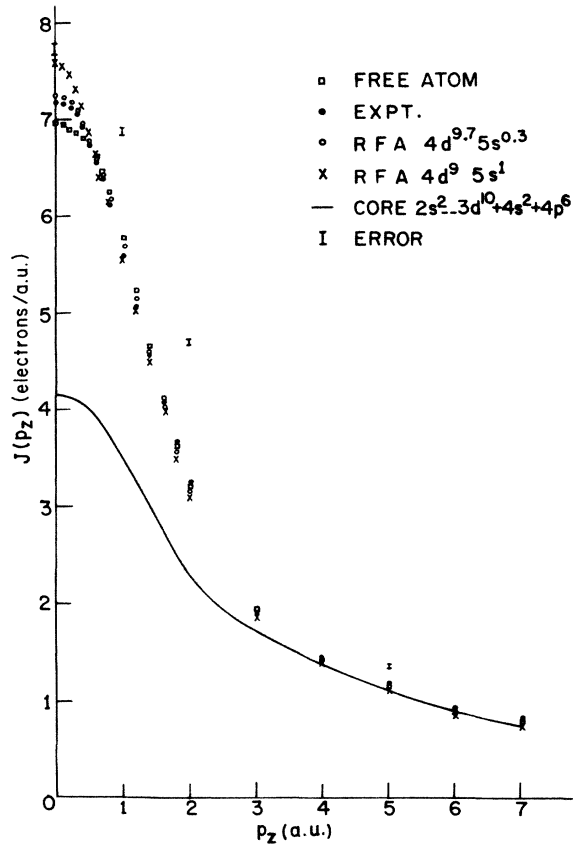

FIG. 3. Comparison of experimental and theoretical Compton profiles for polycrystalline Pd. Theory has been convoluted with the RIF (see text).

Since the core contribution as deduced from the free-atom-model is already close to the experimental contribution, it was logical to conclude that the impulse approximation remains valid for these electrons. Let us now consider this in terms of the binding energy (BE) criterion.[17] The binding energies for L electrons[17] are 3.607, 3.33, and 3.17 keV, while the recoil energy (RE) varies from about 11 to 7 keV as we go from 0 to 7 a.u. Thus, the ratio RE/BE is about 2 and increases to 3 or more for lower p_z values. Thus, the impulse approximation (IA) is reasonably satisfied for the L as well as other electrons. Mendelson and Smith[23] investigated the consequences of nonvalidity of IA for L electrons and have observed that although there may be some difference between IA and non-IA results for individual subshells but in the total contribution of L electrons the deviations are hardly significant. This obviously seems to be happening in this case also.

A useful test for this conclusion comes from the comparison of the present experimental results with those of Podloucky *et al.*[7] (corrected for multiple scattering) from 320 keV γ rays. Although these authors have given a total profile for only the 100 direction, the anisotropies for the principal directions are also given. Their $J(0)$ value is about 7.25, in which the contribution of 1s electron is 0.036. The differences in the various directional values at $p_z=0$ are very small and hence their $J_{100}(0)$ value may be taken as a good estimate of their spherically averaged value for $p_z=0$. Their $J(0)$ value, excluding the 1s contribution, thus comes out to be 7.21, whereas our value was 7.18 ± 0.04, in excellent agreement with their result. For other p_z values the situation is similar and beyond 4 a.u.; both their as well as our data are well represented by the core contribution. This in a way only serves to confirm the above assumption that IA may be considered valid for this case also despite the fact that 60 keV photons were used here. We cannot, however, compare our results with the work of Lässer and Lengeler[12] (LL) because their results were not corrected for the effects of multiple scattering known to change the low-momentum values significantly. LL used radiation of 159 keV and a 0.5-mm thick sample. It has been discussed by Halonen *et al.*[18] that the ratio of total double to single scattering is describable in terms of a parameter λ called effective thickness involving μd (μ being the absorption coefficient for incident beam and d the sample thickness). The value of λ for the LL experimental arrangement comes out to be 0.044 cm^{-1}, whereas for this work this is 0.0086 cm^{-1}. This clearly suggests that their data would contain significant amount of multiple scattering. In our work, despite a much lower value of λ, the correction in the $J(0)$ value was 1.4%, and for their value of λ this correction could easily be about 5%. Their $J(0)$ value is 6.9 and a correction of 5% would bring it close to the value of Podloucky *et al.*[7] and our value. As for the correction due to instrumental resolution, the deconvolution as carried out by the present authors leaves a residual effect [or a residual instrumental function (RIF)] with a full width at half maximum (FWHM) of about 0.4 a.u., which is al-

most close to the FWHM of their instrumental function. Thus their unconvoluted data and our deconvoluted data are nearly equivalent as far as the instrumental broadening effects are concerned.

To determine the valence-electron Compton profile we have subtracted the contribution from core electrons shown by the solid line in Fig. 3. These values are given in Table I. Theoretical results for the two RFA and APW calculations are found in columns 2–5 and the experimental data in column 6. The errors shown for some points actually correspond to the total profile and thus the values represent their upper limit. All these values have been normalized to 4.8329 electrons, being the area of free-atom profile for valence electrons ($4d^{10}$) between 0 and 4 a.u.

It has been often discussed that for the comparison of theory with "deconvoluted" experiment, theory has to be convoluted with the residual instrumental function.[22] In Fig. 4 we show this comparison for the various theoretical results by plotting the difference profile ΔJ ($J_{\text{theory}} - J_{\text{experimental}}$). The theoretical values from Table I have been convoluted with the RIF of our setup (column 7) maintaining the same normalization. Interestingly, the difference profile shows with much clarity the comparison that could be seen in Fig. 3. As seen by Podloucky *et al.*[7] the free-atom values are smaller than experiment initially, but between 0.5 and 1.5 a.u. the situation is reversed and thus suggests the occupation of 5*s*-5*p* bands in the metal. The APW values are somewhat higher than the experimental values in the low-momentum region; but beyond 1.5 a.u. the experimental values are larger. As for the RFA model, the differences even for $4d^9 5s^1$ are very large, and were even larger for $4d^8 5s^2$ (not shown) throughout. For the $4d^{9.7} 5s^{0.3}$ configuration, the difference is quite small up to 0.8 a.u., but increases between 0.8 and 1.8 a.u. It is, in general, close to our APW values for most of the p_z values. In order to determine the most favored configuration, we computed the total deviation ($\sum_0^{7\text{ a.u.}} |\Delta J|^2$) for the various cases.

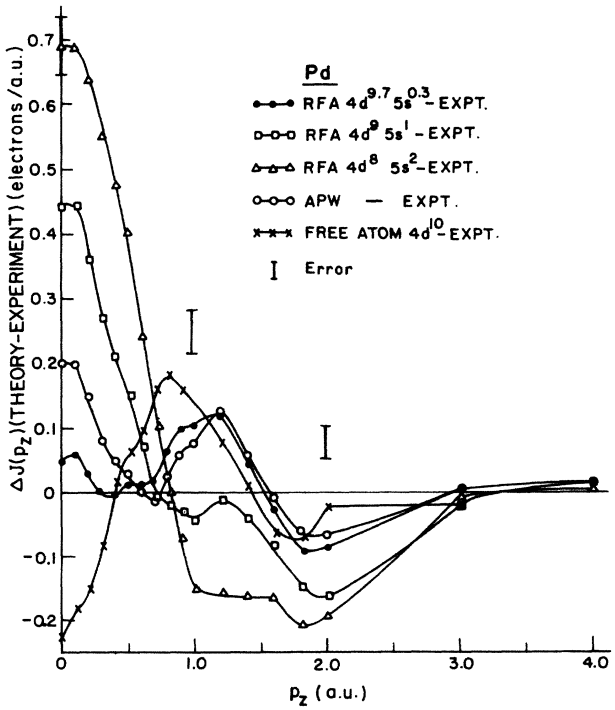

FIG. 4. Difference (ΔJ) profiles for valence electrons in polycrystalline Pd. The theory has been convoluted with the RIF.

It was found that this quantity ($\sum |\Delta|^2$) was lowest for the $4d^{9.7} 5s^{0.3}$ configuration. It may be mentioned that we had, in fact, tried a number of other 4*d*-5*s* configurations, but it turned out that mean-square deviation with respect to experiment was lowest when 0.3 (± 0.1) electrons were assigned to the 5*s* band. Thus, the present study suggests 0.3 ± 0.1 *e*/at. in the 5*s* band and the same number of holes in the 4*d* band. This is indeed interesting because, as mentioned earlier, from de Haas–van Alphen measurements the number of 5*s* electrons in Pd was determined to be about 0.36 per atom which obviously is very close to our conclusions.

Regarding our APW results, we have noticed that our anisotropy values were in good agreement with the earlier work.[7] The APW values given here are already identical to the best RFA values. The possibility of varying the 4*d*-5*s* occupation has resulted in a considerable advantage, combined with the simplicity of obtaining the agreement shown here. Pd metal is a typical case, dominated largely by *d* bands; and perhaps this explains how a simple model such as RFA has worked so well here.

Among other investigations, it is worthwhile to note that Kostroun *et al.*[24] measured the *K*-edge photoabsorption spectra of several 4*d* transition metals and observed that as the *d* band was filled in the row, the shoulder structure around the *K* edge became progressively weaker and disappeared entirely for Ag, which has a filled *d* band. More direct evidence of *d* holes could be seen in the *L*-absorption spectra, because L_2, L_3 transitions correspond to 2*p*-4*d* and 2*p*-5*s* transitions. Measurements of the L_1, L_2, and L_3 edges[25] of Pd show strong peaks at L_2 and L_3 edges but not at L_1, which has a 2*s* initial state. This is easily understood in terms of narrower core-hole width and increased transition rate due to the presence of unoccupied *d* states around the Fermi level. In order to determine the number of holes in the 4*d* band, both EELS (electron-energy-loss spectrum) and XANES (x-ray absorption near-edge structure) can be employed; but the analysis of the results has to be carried out very carefully.

V. CONCLUSION

In this paper we have presented the experimental Compton profile for valence electrons in polycrystalline Pd and compared it with theoretical results from two different approaches, namely, the RFA model and APW method. It is shown that the APW calculation reproduces reasonably the shape of the Compton profile. The RFA model provides a good overall description of the valence-electron Compton profiles when 0.3 ± 0.1 electrons are assigned to the 5*s* band. This is in agreement with the conclusions of dHvA and other studies. This

work once again brings out the efficacy of Compton-scattering studies.

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