

Compton profiles of vanadium and palladium hydrides

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Compton profiles for polycrystalline $\text{PdH}_{0.72}$, $\text{VD}_{0.77}$, $\text{VH}_{0.71}$, Pd, and V have been determined by Compton scattering of 159-keV photons from a $^{123}\text{Te}^m$ source. The difference profiles before and after hydrogen loading are compared to different models for the electronic structure of the hydrides. It is shown that the Compton profile is a sensitive test of the accuracy of various model wave functions for the hydrides. In both palladium and vanadium hydride (deuteride) the anionic model (where it is assumed that the hydrogen forms a negative ion H^- in the hydride) does not describe the experimental results. The best agreement with the experimental data for $\text{PdH}_{0.72}$, $\text{VD}_{0.77}$, and $\text{VH}_{0.71}$ is obtained for a model which is based on band-structure calculations for these hydrides and which takes into account that hydrogen-palladium or hydrogen-vanadium bonding states are created below the Fermi level by the introduction of hydrogen in the host lattice.

I. INTRODUCTION

Metal-hydrogen systems are of great technological and scientific interest. For a basic understanding of the different properties of these systems the electronic structure of the dissolved hydrogen must be known. Band-structure calculations of hydrides have greatly helped to elucidate this problem. Most calculations have been done for Pd hydrides.¹⁻³ These calculations show that the electrons introduced into the lattice by the hydrogen do not fill up the palladium bands according to a rigid-band model. Rather, by the formation of hydrogen-palladium bonding hybrids, states which are filled in pure Pd are lowered in energy and shifted below the Pd d states and some other states which are empty in pure Pd are shifted below the Fermi level. The former have been observed by Eastman *et al.*⁴ and Antonangeli *et al.*⁵ in photoemission experiments. Furthermore, by the introduction of hydrogen, the Fermi level is moved to higher energies and is above the d bands in the compound PdH. A similar behavior in V hydrides has been found in band-structure calculations⁶ and observed experimentally by soft-x-ray emission spectroscopy.⁷

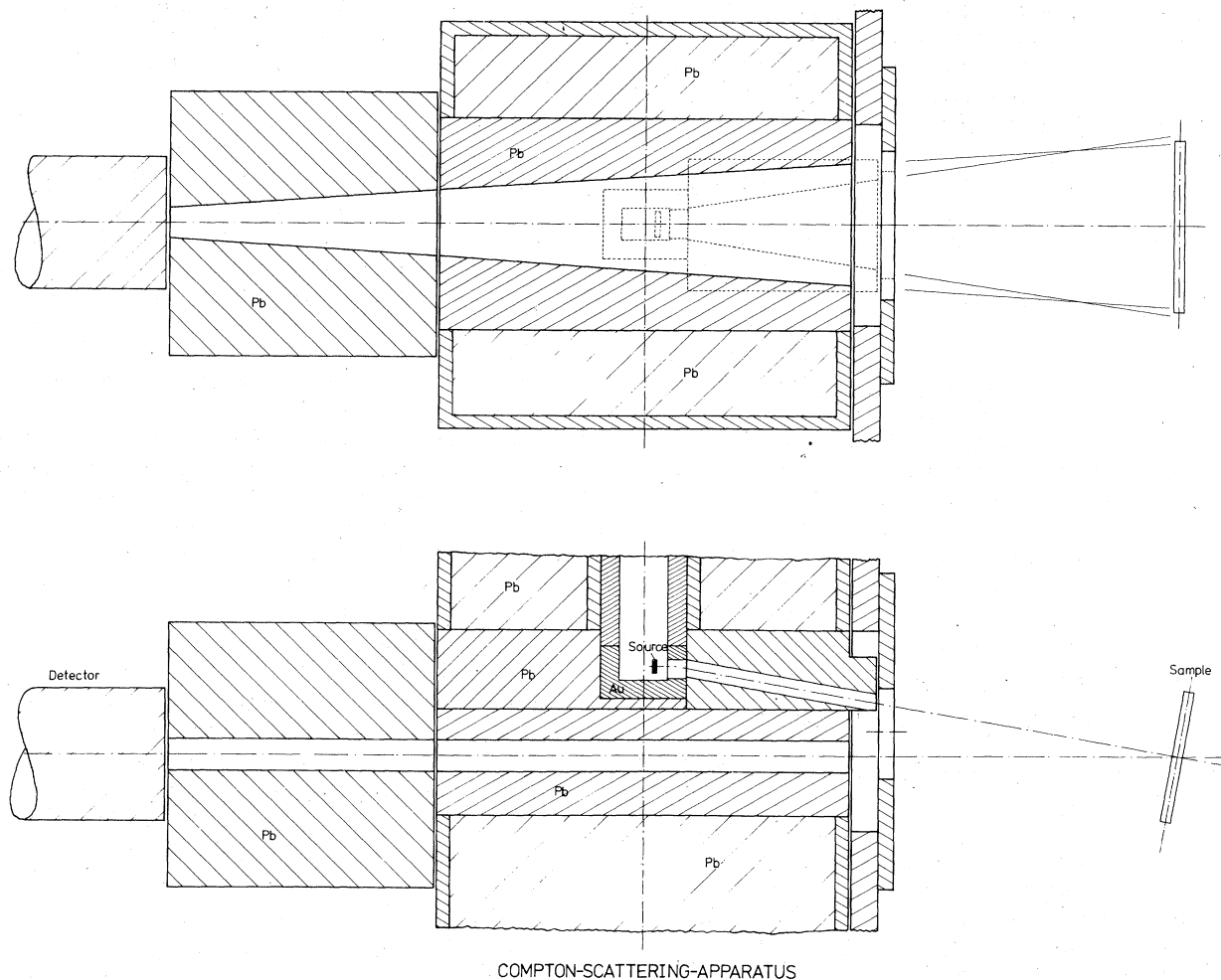
An experimental technique which is especially suited for the determination of the electronic structure of metal hydrides is the Compton scattering of high-energy photons.⁸ It is the electron momentum distribution rather than the electron energy spectrum which is measured by this technique. It will be shown below that the electron momentum distribution is a very sensitive function of the way in which the hydrogen is dissolved in the lattice. Therefore, a determination of the electron momentum distribution in a hydride by means of Compton scattering allows one to discriminate between different models for the hydride structure.

Metal-hydrogen systems are especially suited to be investigated by Compton scattering. Indeed, by measuring the Compton profiles on the same sample before and after hydrogen loading, the contribution of the core electrons can be easily separated from that of the valence electrons, which are the only ones affected by the dissolution of hydrogen.

Compton profiles of metal hydrides have been previously measured on polycrystalline $\text{VH}_{0.45}$,⁹ on single-crystal $\text{NbD}_{0.6}$,¹⁰ $\text{NbH}_{0.76}$,¹¹ and $\text{NbH}_{0.29}$.¹² In this paper, we report Compton profiles measured on $\text{PdH}_{0.72}$, $\text{VD}_{0.77}$, and $\text{VH}_{0.72}$. Section II is a description of the experimental setup. Section III gives the experimental results. In Sec. IV the results of the measurements are compared with different model calculations of the momentum distribution of the conduction electrons in the hydrides investigated.

II. EXPERIMENTAL

Our experimental setup is similar to that used by Eisenberger and Reed.¹³ A $^{123}\text{Te}^m$ source provides 159-keV γ rays. At a mean scattering angle of 171° , the average energy transfer to the electrons is 61 keV, so that the impulse approximation¹⁴ is quite well satisfied even for the strongly bound inner electrons of Pd. A unique feature of the present setup is the use of rectangular beam channels (Fig. 1). The height of the channels was kept constant but their width increased linearly from the source to the sample and from the detector to the sample. This allowed a substantial increase in the counting rate. Since the scattering angle is near to 180° this arrangement does not lead to a significant loss in energy resolution but it does lead to a large spread in the direction of the photon momentum transfer relative to the



COMPTON-SCATTERING-APPARATUS

FIG. 1. Top view and side view of the experimental arrangement showing the rectangular beam channels between source, sample, and detector. In order to obtain a scattering angle as near as possible to 180° without increasing too much the direct radiation from the source to the detector, the source is housed in a gold block.

crystallographic axes of the sample. This type of channel is therefore only appropriate for polycrystalline samples. In order to reduce the back-ground scattering, the samples were attached by needles to a goniometer head and located in an evacuated chamber.

A solid-state detector (intrinsic Ge) was used to analyze the energy of the scattered photons. The electronics [linear amplifier, lineargate stretcher, analog-to-digital converter, and multichannel analyzer (4096 channels)] was temperature and voltage stabilized. The drift was restricted to 0.1 channel over a one-week run. At the position of the Compton peak (98.24 keV for 171°), the resolution of the detector was 446 eV . The angular divergence of the beam increased the overall energy resolution at the Compton peak to 463 eV or 0.400 a.u. ($1 \text{ a.u.} = \hbar/a_0$, where a_0 is the Bohr radius).

The detector efficiency was measured by means of calibrated radioactive standards¹⁵ (^{241}Am , ^{57}Co , ^{133}Ba , ^{152}Eu , and ^{182}Ta). The energy calibration of the multichannel analyzer was made by means of the nuclides ^{241}Am and ^{57}Co , by the position of the $\text{Pb } K\alpha_1$ and $\text{Pb } K\alpha_2$ fluorescence lines from the lead shielding, and from the position of the Rayleigh peak.

The samples used were high purity (99.99%) polycrystalline palladium sheets (0.5 mm thick) and vanadium sheets (1 and 2 mm thick). To avoid passing through the two phase (α - β) regions, the palladium samples were hydrogen loaded at 350°C and a hydrogen pressure of 85 bars. The samples were slowly cooled to room temperature over 3 days. Since Pd forms no oxide layer in air, the samples were stored at 77 K to prevent the hydrogen from escaping. During the measurements of the

Compton profiles, the hydrogen-loaded Pd samples were kept at room temperature and at 1.2 bars hydrogen between two 25- μm mylar windows. The vanadium samples (purity 99.92%) were loaded with hydrogen and deuterium at 550°C and 3000 Torr and cooled to room temperature within 16 h. An oxide layer which forms in air prevents the hydrogen from escaping the samples. Due to the hydrogen loading, the sample lengths changed by 3.6% to 4.5%. The hydrogen concentration was determined by weighting and by heat extraction and was found to be $\text{PdH}_{0.72}$ for the 0.5-mm palladium sheet. The corresponding values for the 1- and 2-mm vanadium sheets are $\text{VD}_{0.77}$ and $\text{VH}_{0.71}$. The concentrations are accurate to $\pm 1\%$. From the phase diagrams of PdH (Ref. 16) and of VD ,^{17,18} our palladium hydride is in the fcc β phase and our vanadium deuteride is in the bcc α' phase. The solutions are homogeneous with no change in the host-lattice symmetry. On the other hand, according to the phase diagram of VH by Schober *et al.*,¹⁹ $\text{VH}_{0.71}$ is in the ϵ phase. Here the host lattice has changed its symmetry from bcc probably to body-centered-tetragonal (bct).²⁰

III. EXPERIMENTAL RESULTS

Figure 2 shows the energy distribution of the photons scattered by polycrystalline $\text{PdH}_{0.72}$. Besides the Compton profile centered at 98.24 keV, one observes the $K\alpha$ and $K\beta$ fluorescence lines of lead shielding, the K edge of Pd at 134.65 keV, and the Rayleigh peak at 159.00 keV. The number of photons counted at the peak of the Pd Compton profiles was after 6 days of data collection 74 000 counts per channel of width 84.3 eV (~ 0.07 a.u.). The corresponding values for the 1- and 2-mm V sheets were after 3 days of data collection 120 000

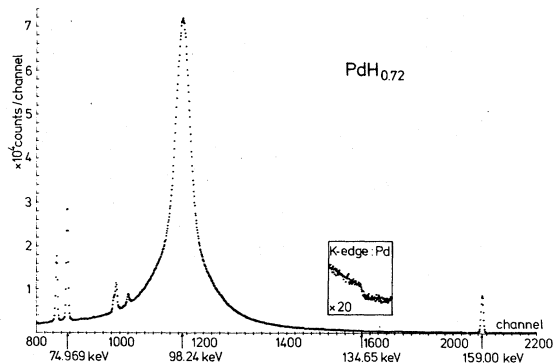


FIG. 2. Energy distribution of 159-keV photons scattered at 171° by polycrystalline $\text{PdH}_{0.72}$. The four lines on the low-energy side of the Compton peak centered around 98.24 keV are the $\text{Pb}K\alpha$ and $\text{Pb}K\beta$ fluorescence lines from the lead shielding.

and 220 000 counts for a channel width of 62.6 eV (~ 0.05 a.u.). The signal-to-noise ratio was reduced from 250 without mylar foils to 30 for the palladium samples encapsulated in mylar foils.

The evaluation of the data was made according to the following procedure. The experimental data were smoothed first by a nine-point least-squares procedure.²¹ The smoothed data are within twice the statistical error of the measured data. The background scattering was measured by removing the sample from the sample chamber. For samples not encapsulated in mylar it turned out to be linear in energy. In the case of the Pd hydride, the background contains an additional contribution from the mylar window in front of and behind the sample. The contribution from the mylar behind the sample was corrected for the absorption of the photons in the sample. The next step was to correct the data for the energy-dependent detector efficiency.¹⁵ The finite energy-resolution function of the detector system was approximated by a Gaussian with energy-dependent width.¹⁵ Using an iterative procedure,²² the experimental data were deconvoluted, but we feel that a convolution of the theoretical data with the energy-resolution function gives a more reliable comparison between the experimental results and the theoretical models explained below.

The correction of the experimental results for the energy-dependent photon absorption $A(E)$ in the sample was made by means of the following expression

$$A(E) = \left[1 - \exp\left(\frac{-d(\mu + \mu')}{\sin \frac{1}{2}\vartheta}\right) \right] \left(\frac{d(\mu + \mu')}{\sin \frac{1}{2}\vartheta} \right)^{-1}. \quad (1)$$

Here, μ and μ' are the total absorption coefficients for the incoming and scattered photon energies and d is the sample thickness. The values of μ and μ' for Pd and V were taken from Ref. 23. The corresponding data for the hydrides were calculated according to the composition of the hydrides. The mean scattering angle ϑ was determined from the position of the Compton peak. The correction for the scattering cross section was made according to Ref. 24. Finally, the energy scale was transformed into the momentum scale and the profiles $J(q)$ normalized according to

$$\int_{-\infty}^{\infty} J(q) dq = Z, \quad (2)$$

where Z is the number of electrons per atom in the pure metals and per MH_x in the hydrides. The integration in Eq. (2) was limited to the high-energy side of the Compton profile and extended from $q = 0$ to $q = 7.0$ a.u. Since the chemical environment of an atom does not affect the electron momenta above $q = 7$ a.u., and since the momentum of the

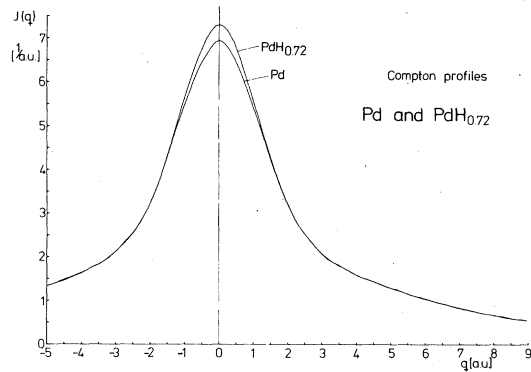


FIG. 3. Normalized nondeconvoluted Compton profiles for polycrystalline $\text{PdH}_{0.72}$ and Pd vs electron momentum q (1 a.u. = \hbar/a_0 ; a_0 Bohr radius).

electron brought into the lattice by the hydrogen atom is expected to be confined to 1 or 2 a.u., we have used the atomic Compton profiles calculated by Biggs *et al.*²⁵ to calculate

$$N = \int_0^{7 \text{ a.u.}} J(q) dq. \quad (3)$$

The values for N obtained are 18.513 for Pd and 10.301 for V. The corresponding values for the hydrides are therefore 18.873 for $\text{PdH}_{0.72}$, 10.686 for $\text{VD}_{0.77}$, and 10.656 for $\text{VH}_{0.71}$.

No correction has been made for multiple scattering. Since we were primarily interested in the difference profile of the hydrides and the corresponding host metals, multiple scattering cancels out in a first approximation. In addition, the samples were thin compared to the mean free path of the photons.

Figure 3 shows our experimental Compton profiles for polycrystalline Pd and $\text{PdH}_{0.72}$. The two profiles differ only in the range between -2 and 2 a.u. which is the range of the momentum of the hydrogen electron. The excellent agreement of the profiles outside 2 a.u. shows that the core electrons of the host atoms are not affected by the hydride formation. The same behavior was also observed in the vanadium hydrides and deuterides. The difference profiles

$$\Delta J(q) = J_{\text{hydride}}(q) - J_{\text{host}}(q) \quad (4)$$

are given in Table I and plotted in Figs. 4 and 5 for polycrystalline $\text{PdH}_{0.72}$ and $\text{VD}_{0.77}$. The experimental profiles are indicated by asterisks. The left-hand side of Fig. 4 shows the nondeconvoluted and the right-hand side the deconvoluted results. The difference profiles for polycrystalline $\text{VD}_{0.77}$ and $\text{VH}_{0.71}$ normalized to the same concentration agree within the error limits.

IV. DISCUSSION

We have compared the difference profiles $\Delta J(q)$ which are attributed to the influence of dissolved hydrogen with four different models for the wave function of the hydrogen electron. In the "protonic" model¹⁰ it is assumed that the dissolved hydrogen atom donates its electron to the conduction band of the host lattice and that, in the case of $\text{PdH}_{0.72}$, it enhances the momentum distribution of the ten conduction electrons of Pd by the factor $10.72/10$, i.e., proportional to the increased number of conduction electrons. In the case of $\text{VD}_{0.77}$ the momentum distribution of the five conduction electrons of V is enhanced by the factor $5.77/5$. It should be

TABLE I. Difference Compton profiles for polycrystalline $\text{PdH}_{0.72}$ and Pd, for $\text{VD}_{0.77}$ and V, and for $\text{VH}_{0.71}$ and V. Any theoretical profile should be convoluted with our Gaussian-resolution function of 0.40-a.u. full width at half-maximum before comparison with the nondeconvoluted data.

q [a.u.]	$\text{PdH}_{0.72}^a$	$\text{PdH}_{0.72}^b$	$\text{VD}_{0.77}^b$	$\text{VH}_{0.71}^b$
0	0.355	0.360	0.388	0.351
0.1	0.362	0.362	0.386	0.349
0.2	0.381	0.374	0.379	0.343
0.3	0.392	0.376	0.362	0.329
0.4	0.377	0.356	0.351	0.314
0.5	0.336	0.321	0.328	0.307
0.6	0.286	0.283	0.301	0.296
0.7	0.242	0.247	0.269	0.259
0.8	0.208	0.213	0.231	0.213
0.9	0.180	0.179	0.192	0.178
1.0	0.146	0.147	0.156	0.153
1.1	0.109	0.115	0.129	0.117
1.2	0.076	0.084	0.110	0.088
1.3	0.055	0.064	0.086	0.072
1.4	0.045	0.053	0.061	0.054
1.5	0.040	0.043	0.045	0.044
1.6	0.033	0.033	0.029	0.032
1.7	0.025	0.025	0.016	0.023
1.8	0.017	0.019	0.014	0.020
1.9	0.014	0.015	0.013	0.018
2.0	0.011	0.011	0.012	0.017
2.1	0.008	0.007	0.012	0.016
2.2	0.006	0.004	0.010	0.015
2.3	0.002	0.001	0.010	0.014
2.4	0	0	0.009	0.013
2.5	0	0	0.009	0.012
2.6			0.008	0.011
2.7			0.007	0.009
2.8			0.006	0.007
2.9			0.003	0.004
3.0			0.001	0.002

^aCorrected for spectrometer resolution.

^bNo resolution correction.

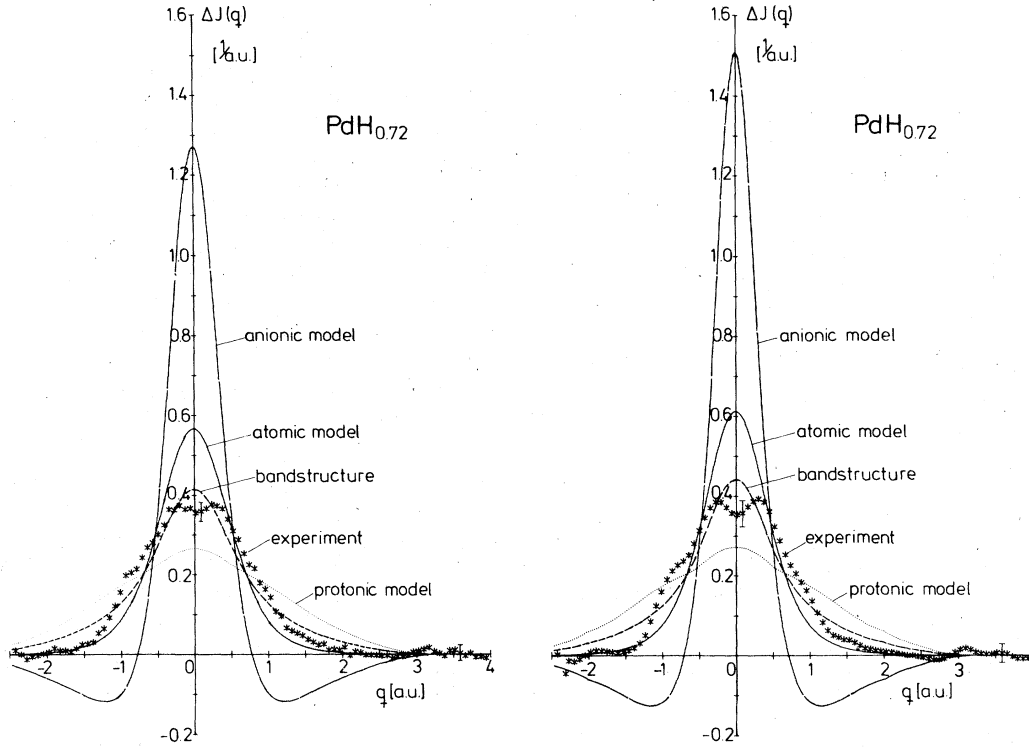


FIG. 4. Difference Compton profiles for polycrystalline $\text{PdH}_{0.72}$ and Pd (*) compared with the profiles for four different model wave functions describing the structure of the hydride. On the left-hand side the model profiles are convoluted with the energy-resolution function and the experimental data are not deconvoluted. On the right-hand side the experimental data are deconvoluted.

emphasized that this is not a rigid-band model because the additional electrons do not shift the Fermi level to higher energies. We have used for $\text{PdH}_{0.72}$ the Compton profile $J_{\text{Pd}}^K(q)$ of the ten conduction electrons of polycrystalline Pd calculated by Kanhere *et al.*²⁶ and calculated the difference profile $\Delta J^+(q)$ for the protonic model according to

$$\Delta J_{\text{PdH}_{0.72}}^+(q) = (10.72/10 - 1)J_{\text{Pd}}^K(q). \quad (5)$$

This profile is shown in Fig. 4. On the left-hand side of the figure, $\Delta J^+(q)$ has been convoluted with the energy-resolution function of the detector system. For the protonic model of V deuteride we have used the Compton profile $J_{\text{V}}^W(q)$ calculated by Wakoh *et al.*²⁷ for the five conduction electrons of V and calculated the difference profiles in a similar way to Eq. (5). The result is shown in Fig. 5. Our model makes no distinction between hydrides and deuterides. The experimental difference profiles for $\text{VD}_{0.77}$ and $\text{VH}_{0.71}$ agree with one another (if normalized to the same hydrogen or deuterium concentration). In the following we confine ourselves to the system $\text{VD}_{0.77}$ since in this system the host lattice undergoes no phase transition by deuterium loading.

In the "anionic" model, we assume that the hydrogen removes an electron from the conduction band of the host lattice and forms a negative ion H^- . Assuming for this ion a hydrogenlike wave function²⁸

$$\Psi(r) = (\alpha^3/\pi a_0^3)^{1/2} \exp(-\alpha r/a_0), \quad (6)$$

with $\alpha = 11/16$ and calculating from this the corresponding momentum wave function by Fourier transformation one can find in a straightforward manner the Compton profile for the ion H^- ,

$$J_{\text{H}^-}(q) = (16/3\pi\alpha)[1 + (q/\alpha)^2]^{-3}. \quad (7)$$

The difference profile for the "anionic" model of $\text{PdH}_{0.72}$ is, therefore

$$\Delta J_{\text{PdH}_{0.72}}^-(q) = 0.72 J_{\text{H}^-}(q) - \Delta J_{\text{PdH}_{0.72}}^+(q). \quad (8)$$

The negative term on the right-hand side of Eq. (8) takes into account the electron removed from the conduction band of Pd. The difference Compton profiles for the anionic model of $\text{PdH}_{0.72}$ and $\text{VD}_{0.77}$ are shown in Figs. 4 and 5. The negative values of the difference profile above 1 a.u. are an artifact of the model without physical significance. It is clearly seen from these figures that the anionic

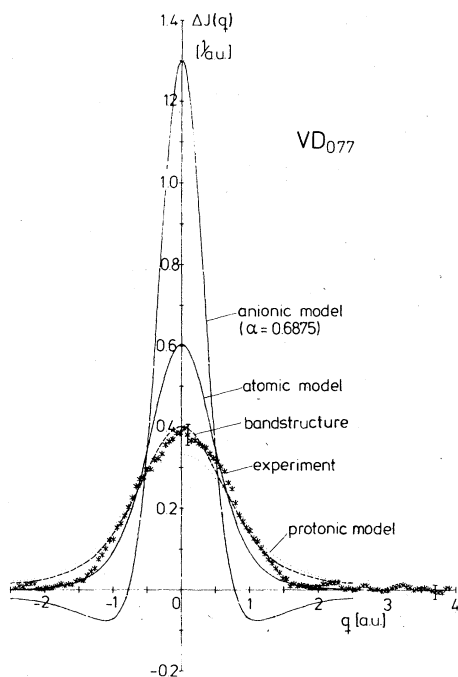


FIG. 5. Nondeconvoluted difference Compton profiles for polycrystalline $VD_{0.77}$ and V (*) compared with the convoluted profiles for four different model wave functions describing the structure of the deuteride.

model is not appropriate to describe the structure of vanadium and palladium hydrides.

In a third model it is assumed that the hydrogen is dissolved as neutral hydrogen atoms. The Compton profile of a hydrogen atom is given by

$$J_H(q) = \frac{1}{2} J_H^-(q; \alpha = 1). \quad (9)$$

The difference profile for the "atomic" model of $PdH_{0.72}$ is, therefore,

$$\Delta J_{PdH_{0.72}}^0(q) = 0.72 J_H(q). \quad (10)$$

This type of model must be excluded for V and Pd hydrides according to NMR measurements which did not show the strong Knight shift to be expected from the bound $1s$ hydrogen electron in the proton resonance.^{29,30} Nevertheless, the model is shown in Figs. 4 and 5 because it shows, in connection with the other models, the sensitivity of the momentum distribution and Compton profiles for various models describing the structure of metal hydrides. It is not expected that the crude models used here can explain the experimental data correctly. Nevertheless, the anionic model can clearly be ruled out for Pd and V hydrides. This is in agreement with the band-structure calculations for the Pd and V hydrides mentioned above.^{1-3,6} Pattison *et al.*¹⁰ come to the same conclusion in the analysis of their niobium hydride data which

they have explained by models similar to the ones used here.

A more appropriate way to calculate the Compton profile of a hydride is to derive it from the wave functions obtained from a band-structure calculation of the hydride. Unfortunately, in the band-structure calculations published so far, only the energies were given but not the wave functions or even the Compton profiles. Nevertheless, some information can be obtained from the currently available band structures. Indeed, the calculations by both Switendick¹ and Papaconstantopoulos *et al.*³ show that the newly created hydrogen-palladium bonding states appearing below the Fermi level can accommodate 0.5 electrons per hydrogen atom. The bonding states have s character about the octahedral hydrogen sites and p character about the Pd sites. In addition, 0.36 electrons per palladium atom are needed to fill up the palladium $4d$ band. Therefore, we assume in our fourth model for $PdH_{0.72}$ that among the 0.72 electrons added per Pd atom, 0.36 electrons are accommodated by the bonding states. Their wave functions are approximated by a free hydrogen atom wave function. This wave function is s -like about the proton and p -like about the Pd for octahedrally located hydrogen. The remaining 0.36 electrons are added to the palladium $4d-5s$ states. For lack of better wave functions their Compton profile is approximated by that of the conduction electrons of metallic palladium calculated by Kanhere *et al.*²⁶ The difference profile $\Delta J^{BS}(q)$ for this fourth model is

$$\Delta J_{PdH_{0.72}}^{BS}(q) = 0.72 \left[\frac{0.5}{10} J_{Pd}^K(q) + 0.5 J_H(q) \right], \quad (11)$$

with $J_H(q)$ taken from Eq. (9). It turns out to be the mean of the atomic and protonic model for the present hydrogen concentration. The corresponding Compton profile is shown in Fig. 4 and labeled "band structure." Although it is based on approximate wave functions, it takes into account the basic features of the band-structure calculations of Pd hydride. It is therefore not surprising that it fits the experimental results the best. Band-structure calculations by Switendick⁶ show also for V hydride that new bonding vanadium-hydrogen hybrids are formed below the Fermi level. They can accommodate about 0.25 electrons per H atom. The remaining electrons shift the Fermi level to higher energies. So the difference profile for the band-structure model of $VD_{0.77}$ is

$$\Delta J_{VD_{0.77}}^{BS}(q) = 0.77 \left[\frac{0.75}{5} J_V^W(q) + 0.25 J_H(q) \right]. \quad (12)$$

This result is shown in Fig. 5 and labeled "band structure." Again it gives the best agreement with the experimental results.

An interesting aspect of the band-structure cal-

culations by Switendick on metal hydrides is that in niobium nearly no states which are empty in the pure metal are shifted below the Fermi level by the introduction of hydrogen.³¹ This is in contrast to Pd and V hydrides. Consequently, practically no additional electrons can be accommodated below the Fermi level in niobium hydride in contrast to palladium and vanadium hydride. Therefore, in NbH the protonic model is expected to be fulfilled much better than in the case of PdH and VH. This is indeed what Pattison *et al.*¹⁰ have observed. These authors were able to explain their experimental difference profile in a satisfactory way by the "protonic" model explained above.

V. CONCLUSION

Compton-profile measurements are a sensitive test for the accuracy of various model wave functions of the conduction electrons in a metal. Since single-crystal samples are not needed, the technique can be applied in those cases where difficult sample preparation makes other techniques unsuitable. Metal-hydrogen systems are especially

appropriate for this technique since the core-electron contribution to the Compton profiles is easily eliminated by measuring the profiles before and after hydrogen loading. In both Pd and V hydride, the anionic model which assumes the structure of the hydrogen to be an anion H^- does not fit the experimental data. Rather these hydrides must be treated in a band-structure approach. Indeed, the palladium- and vanadium-hydride data are explained satisfactory in a model which is based on band structure calculations by Switendick^{1,6} and Papaconstantopoulos *et al.*³ and which takes into account the metal-hydrogen bonding hybrids formed below the Fermi level. If, in addition to the energies, the wave functions were evaluated from these band structures our data could provide a sensitive check for the accuracy of these calculations.

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