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To cite this version:

G.D. Boulakis. Comparison between the experimental Compton profiles of Ti and TiH1.98. Journal de Physique, 1986, 47 (9), pp.1523-1526. <10.1051/jphys:019860047090152300>. <jpa-00210350>
Comparison between the experimental Compton profiles of Ti and TiH$_{1.98}$

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(Reçu le 18 février 1986, révisé le 23 avril, accepté le 15 mai 1986)

1. Introduction.

Metal hydrogen systems are of great scientific and technological interest due to our need in understanding the way gases dissolve in metals, the possible use of hydrogen as fuel, and the use of metals as storage media of hydrogen [1-3]. For the better understanding of the different properties of these systems the electronic structure of the dissolved hydrogen must be known. In recent years, most of the investigations have been done in this direction, i.e. on the transition metals and the rare earth hydrides [4-11].

Compton scattering of high energy photons [12] is especially suited for the determination of the electronic structure of metal hydrides. The electron momentum distribution which is measured by this technique is a very sensitive function of the way in which the hydrogen is dissolved in the lattice. This allows one to determine the validity of different models for the hydride structure. Indeed, by measuring the Compton profiles of the same sample before and after hydrogen loading, the contribution of the core electrons can be separated more or less from that of the valence electrons, which are the ones mostly affected by hydrogen dissolution [4, 13].

The models that have been used in the past for the interpretation of hydrides are: the protonic model [14], where hydrogen donates its electron to the metal conduction band, the anionic model, where an electron is removed from the metal conduction band and forms a hydrogen anion, and the atomic model [15], where the dissolved hydrogen remains neutral.

Titanium is a metal which can absorb large quantities of hydrogen [16] forming hydrides which have been extensively studied because of their special physical aspects [17-24]. From the phase diagram of the titanium-hydrogen system [25, 26] it is evident that at room temperature there are more than one phases except in the region bound by 1.5 $\leq x \leq$ 1.8 (for the TiH$_x$ system) that is characterized as gamma phase.

In this work the Compton profiles of the polycrystalline Ti and TiH$_{1.98}$ are measured at room temperature. The calculated difference of the profiles is compared with the different theoretical models for the electronic structure of TiH$_{1.98}$. It is shown that the Compton profile is a sensitive test of the accuracy of various model wavefunctions for the hydrides. The best fit to our experimental data is given by a model based on self-consistent band structure calculations. In this model the Compton profile is completely defined through the wavefunctions of the system.
a 5 mm thick crystal of 100 mm^2 effective area) and a multichannel analyser (M.C.A.). The main shaping amplifier coupling the detector to the M.C.A. was adjusted to give a channel spacing of 13.46 eV (0.024 momentum a.u.). The scattering angle in the sample chamber was (173.5 ± 1.5°). The detector resolution was 330 eV FWHM at the energy of the Compton peak (48.37 keV at 173.5°). The angular divergence of the beam produced an additional resolution broadening, leading to a total resolution at the Compton peak of 342 eV FWHM or 0.60 a.u. [9, 29]. The system was calibrated with the K fluorescence lines of Tb.

The sample consisted of Ti powder (99.98% pure) which was placed on a rectangular brass frame held in place by 0.001" thick mylar sheets. The thickness of the (powder) samples was 6 mm. A portion of the same Ti material was hydrided by appropriate heat treatment in H_2 gas. After measuring the hydride's Compton profile, two typical samples were weighed, then dehydrided by heating in vacuum and reweighed to determine their composition. The latter was found to be TiH_{1.98}. X-ray [30] and neutron diffraction [31] studies have shown that the TiH_{1.98} compound (mainly gamma phase) has a face-centred cubic (f.c.c.) fluorite type structure, in which the hydrogen occupies sites with a regular tetrahedral symmetry [32]. The observed f.c.c. lattice distortion led to the calculation of the parameter ratio c/α = 0.996. The lattice constant found for this compound was α = (4.466 ± 0.005) Å. Each Compton profile measurement lasted for three full days and accumulated about 1.9 × 10^5 counts/channel in the region of the profile peak for Ti and 2.5 × 10^5 counts/channel for TiH_{1.98}.

The raw data were smoothed and the background, which was measured after removing the powder from the sample holder, was subtracted. The background is not linear in energy because of an additional Compton contribution from the mylar sheets and the brass frame. All samples were enclosed in this frame and no additional corrections for background absorption have been made. Other corrections were also made for the absorption of photons in the sample and the Compton cross section according to references [4, 12]. No corrections for multiple scattering, detector efficiency and instrumental resolution were made. Especially, as far as multiple scattering is concerned, it is known that it lowers the Compton profile at low q values and increases it at higher ones [6, 33, 34]. Such corrections have been published for polycrystalline Ti in references [35, 36]. Yet in our case, although our samples were thick enough to produce such an effect, we do not have to make any corrections because we have analysed only differences in Compton profiles of similar samples of pure Ti and TiH_{1.98}. The multiple scattering contribution of each sample is not considered to present any substantial deviation in magnitude.

In our experimental procedure the finite instrumental resolution function was approximated by a Gaussian with a FWHM of 0.60 a.u. Finally the energy scale was transformed into momentum scale so that the area under each profile, up to a momentum of 7.0 a.u., was normalized to the appropriate free atom value. The profile areas between 0.0 and 7.0 a.u. (9.9 in the case of Ti and 10.89 for TiH_{1.98}) were taken from tables of free atom profiles [15], interpolated with cubic spline functions at intervals of 0.1 a.u. However the 9.9 normalization factor is not so critical because only the difference between the profiles was of interest to us in this study.

3. Discussion.

The difference between the two experimental Compton profiles of TiH_{1.98} and Ti is clearly confined to the valence electron profiles in the low momentum region as shown in figure 1. Figure 2 displays the difference of the Compton profiles found in this work, as well as, the profiles predicted by theoretical calculations. Two error bars in the experimental profile are due to statistical errors.

In the protonic model it is assumed that the dissolved hydrogen atom donates its electron to the conduction band of the host lattice and in the case of TiH_{1.98} it enhances the momentum distribution of the four conduction electrons of Ti by a factor of 5.98/4. It should be emphasized that the so-called protonic model does not result from a shift in the Fermi level according to the rigid band model but from the bare enhancement of the momentum distribution. From the Compton profile J_T(q) of the four conduction electron of polycrystalline f.c.c. structured Ti [28], we can calculate the difference profile ΔJ^+(q) for the protonic model of TiH_{1.98} according to the formula

\[ ΔJ_{TiH_{1.98}}^+(q) = (5.98/4 - 1) J_T(q). \] (1)

F.c.c. band structure calculations for Ti were utilized as a first approximation in this case, since it is expected that the corresponding h.c.p. structure calculations would lead to similar results [28].

![Fig. 1. — The γ-ray Compton raw experimental data for polycrystalline TiH_{1.98} (solid line) and Ti (dashed line).](image-url)
In the anionic model, we assume that a hydrogen atom removes an electron from the conduction band of the host lattice and forms a negative H⁻ ion. Using a hydrogenlike wavefunction [37]

\[
\psi(r) = (\alpha^2/\pi \alpha^0)^{1/2} \exp(-\alpha r/\alpha_0),
\]

with \( \alpha = 11/16 \) and applying a Fourier transformation we get the Compton profile for the H⁻ ion

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

The difference profile for the anionic model of TiH₁.₀₈ is therefore

\[
\Delta J_{\text{TiH}1.08}(q) = 1.98 J_{H^-}(q) - \Delta J_{\text{TiH}1.08}(q).
\]

The negative term in the right hand side of equation (4) takes into account the electron removed from the conduction band of Ti.

From the results plotted in figure 2, it appears that the so-called protonic model agrees better with the experimental data than the anionic model. On the other hand, in the hydrides of early transition metals it has been established that charge transfer occurs from the metal to the H atom. Although these two observations might appear contradictory, this is not so actually. According to reference [38] the charge transfer behaviour determines the type of bond in a given substance, while it cannot be an argument for either the protonic or the anionic model.

Finally, in the atomic model, the dissolved hydrogen is assumed to behave as a neutral atom. In this case its Compton profile is given by

\[
J_{\text{H}}(q) = 1/2 J_{\text{H}}(q; \alpha = 1)
\]

and the difference profile is therefore

\[
\Delta J_{\text{TiH}1.98}(q) = 1.98 J_{\text{H}}(q).
\]

The above mentioned models ignore the lattice expansions which are observed upon hydrogen formation.

On the other hand, the band structure curve is calculated from the data of reference [28]. It should be noted that the theoretical profiles corresponding to the four models have been convoluted with the instrumental resolution function. Furthermore we assumed that the f.c.c. to f.c.t. lattice distortion which is observed in TiH₁.₀₈ [13, 20, 30] because of its low magnitude, does not contribute to the Compton profile of the hydride. These approximations allow the comparison of the TiH₁.₀₈ and Ti profiles and therefore strengthen our ability to draw conclusions about the hydrogen dissolution in the host metal.

In the contrast to some earlier works [38-42], recent [27, 28] theoretical calculations, based on a self-consistent augmented plane wave (APW) band structure method, compute both energies and wavefunctions of the TiH₂. This method is outlined in reference [27] and one should refer to it for details. In this work the discussion is centred around the main conclusions that are derived from the study of the energy bands in TiH₂. In comparison to previous non-self-consistent theoretical band structure methods [38-42] the above mentioned method finds quantitative differences in the ordering of energy levels, the density of states at the Fermi level and the characteristic bandwidths. It is shown that at low energies this dihydride is characterized by two bands (unlike pure Ti). The lowest band (which corresponds to the lowest band of the host metal and appears lower in energy because of the presence of hydrogen) originating at point \( \Gamma' \), represents the Ti-H bonding state. The set of bands centred at the levels \( \Gamma_{25'} \) and \( \Gamma_{12} \) corresponds to the d levels of titanium. The \( \Gamma_{25'} \) level results from the antibonding combination of the two hydrogen atoms in the unit cell. The position of level \( \Gamma_{25'} \) in those results is above the d states at \( \Gamma_{25'} \) and \( \Gamma_{12} \) and is also above the Fermi level \( E_F \) while in the non-self-consistent calculations it is found below the d states. Partial wave analysis of the wavefunctions of \( \Gamma_{25'} \) reveals that we have, approximately, 70 % H s and 10 % Ti f character inside the Muffin-Tin spheres. The way of calculating the Compton profile of this hydride from
its wavefunction is described analytically in reference [28]. In it, there is enough information about the anisotropies of the Compton profiles of Ti and TiH₂.

4. Conclusion.

Compton profile measurements are a sensitive test for the accuracy of various model wavefunctions for the conduction electrons in metals. Indeed, the experimental data for titanium hydride TiH₁.₉₈ are explained satisfactorily by a model which is based on band structure calculations [27, 28]. These calculations explain the mechanisms of hydrogen dissolution in Ti and the modifications of the metallic energy bands due to the introduction of hydrogen. It would have been of interest to measure the difference profile in different directions in single crystals of Ti and TiH₀₉ because this might provide further information on the electron momentum distribution. This is not possible with the present powder targets.

Acknowledgments.

The author wishes to express his appreciation to Prof. N. G. Alexandropoulos for proposing this project and making available the lab. facilities. Thanks are also due to Mrs. C. Alexandropoulos for her help in computer programming, Dr. N. Papanicolaou for helpful discussions on the band structure calculations and Mr. K. Pappas for his technical assistance. The author also wishes to thank the unknown referee for his constructive suggestions.

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