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Extracting the electronic structure of light elements in bulk materials through a Compton scattering method in the readily accessible hard X-ray regime

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Our Compton profile measurements of Ti and TiH2 using readily available hard X-ray radiation at 27.5 keV, detected by both a Hitachi Vortex silicon-drift detector (SDD) and a high-resolution superconducting Transition-edge sensor (TES) array, are found to be in excellent accord with state-of-the-art Density Functional Theory (DFT) based calculations. The spherically averaged difference between the Compton profiles of TiH2 and Ti is well described by an inverted parabola, supporting an itinerant behavior of the electron gas screening the protons in the Ti matrix. Our experimental approach, validated by two different detectors, extends the applicability of Compton scattering technique to the readily accessible hard X-ray regime (below 30 keV). Our study suggests possibilities for experiments at low-flux bending magnet synchrotron beamlines, and pave the way for the development of tabletop Compton experiments with X-ray tubes.

Compton scattering, a fundamental interaction between X-rays and electrons, offers valuable insights into composition and electronic structure of materials. To induce dominant Compton scattering in transition metals such as Ti, a photon beam with an energy of approximately 100 keV is necessary, as illustrated in Fig. 1. Typical Compton experiments are executed with high-flux beams generated with synchrotron sources. Our objective is to utilize hard X-rays below 30 keV (experimentally accessible even with X-ray tubes) to investigate the influence of light atoms on transition metal compounds for which fluorescence is not an issue. Previous Compton scattering experiments on titanium and zirconium hydrides have revealed the sensitivity of the Compton profile to hydrogen in these metals. Examination of the shape of the Compton profile, influenced by low-momentum electrons in the hydrides, facilitates interpretation through the analysis of Compton profile differences, in which many errors are canceled. Combining this experimental strategy with accurate first-principles modeling provides a tool for investigating the influence of light chemical elements in materials.

Our choice of Ti and TiH2 for this study is motivated for several reasons. Ti is well-known to exhibit a remarkable capacity to absorb hydrogen. Hydrogen plays a crucial role in energy storage applications and in including fascinating properties in transition-metal hydrides, including superconductivity. Ti alloys are used extensively in structural components of the hydrogen infrastructure. Our study thus represents a significant advancement in the applications of the Compton scattering technique as well as in the understanding of the electronic structure of TiH2.

We collected spectroscopic data from a Ti metal foil with HCP crystal structure, with dimensions 10 mm × 10 mm × 0.5 mm, and TiH2 powder, retained in a Kapton film, with approximately the same outer dimensions. The samples were illuminated by a 27.5 keV monochromatic X-ray beam generated by reflecting the Advanced Photon Source (APS) 1-BM bending magnet radiation off a Si(111) double-crystal monochromator. Each sample in turn was mounted free-standing in the beam path (in air), illuminated with a beam of cross-sectional area of 5 mm (vertical) × 1 mm (horizontal), and rotated about the vertical axis by 45° from directly facing the incident beam. This angled the sample towards two detectors also in the horizontal plane, both measuring simultaneously – a 96-pixel superconducting Transition-edge sensor (TES) array (fabricated at NIST-Boulder) at a 87.5° photon scattering angle and a single-element Hitachi Vortex silicon-drift detector (SDD) at 138°. The scattering angles were determined by fixing the measured Compton peak to be centered...
on $p_z = 0$ a.u., slightly adjusted from the initial experimental setup of approximately 90° and 140°. The distance from the sample to the active surface of either detector was 250 mm. In order to reduce the proportion of detected photons from lower-energy fluorescence relative to higher-energy Compton scattering, two layers of 0.1 mm thick Al foil were placed in front of each detector. Each sample was measured for approximately 6 hours at a constant count rate, allowing for the collection of $> 5 \times 10^8$ integrated photon counts by the TES array and $> 4 \times 10^7$ integrated counts by the SDD. We estimate from ion-chamber readings the total flux incident on the sample as $2.5 \times 10^{10}$ photons/second, a figure also achievable with sealed X-ray tube sources\textsuperscript{13,14}. Further description of a similar Compton experimental setup and TES instrument is given in Patel et al.\textsuperscript{15}

Determining the central energy of the Compton peak was aided by fitting a model consisting of a Laplace (double-exponential) added to a Gaussian function, an approximation of the convoluted function Van Gysel et al.\textsuperscript{16} found to be the best match to a typical Compton profile shape. Contributions to the total experimental momentum resolution $\sigma_p$ for each detector were estimated as in Table I. Note that the $\sigma$ values quoted here and the Full-Width-at-Half-Maximum (FWHM) values are related by $\text{FWHM} = 2 \sqrt{2 \ln 2} \ \sigma$. Detector energy resolutions were obtained by fitting a Gaussian to the elastic peak in the measured spectrum. The incident energy resolution was set to $\Delta E/E = 1.5 \times 10^{-4}$ based on the Darwin width of the Si (111) reflection. We found the total momentum resolution for the TES detector to be dominated by the angular contribution due to its positioning at approximately 90° and its larger field of view (wider than in Patel et al.\textsuperscript{15} due to different collimation), while for the SDD the overall momentum resolution was dominated by the detector energy resolution.

Theoretical models of the Compton profiles were convoluted with a Gaussian function of width $\sigma = \sigma_p$ prior to comparison with the experimental data. The experimental profiles were normalized so that the total areas between $p_z = -4$ to 4 a.u. were equal to the area over the same range of the corresponding theoretical DFT-based profiles, which were themselves normalized over a large momentum range so that their total areas were equal to the total number of electrons involved ($Z = 22$ for Ti and $Z = 24$ for TiH$_2$).

The TES array data was further scaled up by 5% to account for the presence of Ti Z-line escape peaks overlapping the Compton peak. No multiple-scattering, background subtraction or other corrections to the measured profiles were applied, and no other free parameters were used in the analysis. The probability of multiple scattering is proportional to the optical thickness of the sample\textsuperscript{17} – approximately 1.5 attenuation lengths in our case – and so will affect our measured profiles. However, since our samples have the similar thickness, similar density, and the corrections due to multiple scattering are broad relative to the main Compton profile (smoothing over differences due to the sample composition), we expect multiple scattering contributions to largely cancel out when we consider the difference Compton profiles. A powder X-ray diffraction measurement of the TiH$_2$ sample returned a lattice parameter value of 4.450 Å compared to the literature value\textsuperscript{18} of 4.41 Å, and supported the FCC structure used in our modelling, see Fig. S1 in Supplemental Materials.

The collected spectra were transformed into momentum space via the formulation of Ribberfors\textsuperscript{19}. Within the impulse approximation\textsuperscript{20}, the double-differential cross-section is:

$$
\frac{d^2 \sigma}{dp dp'} = F \cdot J(p_z),
$$

where the explicit form of $F$ that accounts for relativistic effects is given by Ribberfors\textsuperscript{19}. Failure of the impulse approximation produces an asymmetry in the experimental Compton profile as shown in Huotari et al.\textsuperscript{21} We find only a very slight asymmetry about $p_z = 0$ in our measured Compton profiles, which we attribute to the background and not to the Compton profile itself, as illustrated in Fig. S2 in the Supplementary Materials. The Compton profile $J(p_z)$ is given in terms of the ground-state electron momentum density $\rho(p)$ by the formula\textsuperscript{22}.

$$
J(p_z) = \int \rho(p) \, dp_1 \, dp_2,
$$

where $p = (p_x, p_y, p_z)$ is the electron momentum, and $p_z$ is taken to lie along the direction of the scattering vector. The

![Figure 1](image-url)
electron momentum density can be expressed as
\[
\rho(p) = \sum_{j} \left| \Psi_{j}(r) \right|^2 \exp(-i \mathbf{p} \cdot \mathbf{r}) d^3 \mathbf{r},
\]  
(3)
where an independent particle approximation is assumed.
Core electron states of Ti and H were described by Hartree-Fock (HF) orbitals provided by Biggs et al.\textsuperscript{23} Valence electronic structure modifications of Ti and TiH\textsubscript{2} were obtained via \textit{ab initio} DFT-based calculations using the Projector-Augmented-Wave (PAW) method\textsuperscript{24} as implemented in the Vienna Ab initio Simulation Package (VASP)\textsuperscript{25-26} with an energy cut-off of 520 eV. Exchange-correlation effects were treated using the generalized gradient approximation (GGA), parametrized by Perdew, Burke, and Ernzerhof (PBE)\textsuperscript{27}. A variant, PBE functional revised for solids, (PBEsol)\textsuperscript{28}, can improve the description of certain electronic properties. However, Sharma et al.\textsuperscript{29} have shown that the corrections for the Compton profiles using PBEsol (compared to local density approximation and therefore to PBE) are marginal. Therefore, we opted to use PBE, which is preferable in general over PBEsol. The crystal structure and the ionic positions were optimized using a force convergence criterion of 0.01 eV/Å for each atom, along with a total energy tolerance of 10\textsuperscript{−5} eV. For the Ti metal, we employed the standard HCP structure with a 2-atom primitive cell, characterized by \(a = b = 2.94 \text{ Å} \) and \(c = 4.64 \text{ Å}\). For TiH\textsubscript{2}, we used the FCC structure proposed by Shanavas et al.\textsuperscript{30}, with a unit cell containing 12 atoms and an equilibrium lattice constant \(a = 4.41 \text{ Å}\). The Brillouin zone was sampled using a uniform \(\Gamma\)-centered \(7 \times 7 \times 7\) k-point grid. Within the DFT framework, the spherically-averaged electron momentum density was calculated with Kohn-Sham orbitals following the methodology of Makonen et al.\textsuperscript{31}

In addition to atomic Hartree-Fock and DFT calculations, we consider two simple models to gain physical insight into the fate of the electron associated with the hydrogen atom. In the \textit{screened model},\textsuperscript{3} the influence of the host metal is incorporated by screening the proton with an effective charge \(Z\). The wavefunction of the electron screening the proton is then given by \(\psi(r) = Z^2/\pi \exp(-Zr)\), and the corresponding Compton profile (normalized to \(Z\)) is
\[
J(p_z) = \frac{8Z^5}{3a(p_z^2 + Z^2)^{3/2}},
\]  
(4)
In the \textit{free electron model},\textsuperscript{2} the electrons donated by the H atoms form a non-interacting free-electron gas. In this case, the electrons occupy all available energy levels up to the Fermi energy \(E_F\). Since the energy band is given by \(E(p) = p^2/2m\), the occupied states form the Fermi sphere, with the radius of the Fermi momentum \(p_F = (3\pi^2 n)^{1/3}\), and the Compton profile per electron is given by
\[
J(p_z) = \begin{cases} 
\frac{5}{2}(p_z^2 - p_z^4)/4p_F^2, & \text{if } |p_z| < p_F, \\
0, & \text{otherwise}.
\end{cases}
\]  
(5)
Figure 2 displays our raw SDD and TES spectra, where the contribution from fluorescence, Rayleigh, and Compton scattered radiation are observable. These spectra are based on broadband energy-dispersive instruments in which the entire energy range is recorded in one measurement. Inelastic Compton scattering leads to a decrease in the energy of the X-ray, which depends on the scattering angle, and since our two detectors were at different positions, the Compton peaks lie at different energies in the measured spectra. Even with the Al foils acting as a high-pass filter, a significant proportion of the total counts recorded are fluorescence, primarily from Ti in the sample, but also some Cu and Zn background from the sample mount and detector housing. In a synchrotron environment, we are photon-rich and primarily limited by our detector maximum count rates; therefore, it is beneficial to filter out the scattered photons that do not contribute to the experiment. In a benchtop setup, for example, where an X-ray tube is used for illumination, one is more likely to be limited by the source flux, and filters may not be needed.
This study addresses questions identified in previous studies by Alexandropoulos et al. in the screened-atomic model by Fujimori and Tsuda, which accommodates 2 electrons per titanium atom in TiH

3

(3)

(2)

(1)

(0)

(−1)

(−2)

(−3)

(−4)

(−5)

(0)

(1)

(2)

(3)

(4)

(5)

FIG. 3. Compton profiles of (a) Ti and (b) TiH measured with a superconducting Transition-Edge Sensor array (solid, in both plots) compared with theoretical models convoluted with a Gaussian of width σ = 0.4 a.u. Compton profiles of (c) Ti and (d) TiH measured with a silicon-drift detector (solid, in both plots), compared with theoretical models convoluted with a Gaussian of width σ = 0.4 a.u. Theoretical plots are based on our DFT computations (dashed) and free-electron Hartree-Fock model (dotted), with two possible electronic configurations of TiH (see main text). Experimental data are plotted with Poisson (\(\sqrt{N}\)) error bars, in (a) and (b) only every 3 points for clarity.

FIG. 4. Difference profile \(\Delta[p_z]\) [TiH - Ti] measured with a superconducting Transition-Edge Sensor array (solid, in all plots), compared to the corresponding calculations: (a) using the DFT methods of this paper (dashed); (b) using two possible electronic configurations of TiH (see main text), and the free-electron Hartree-Fock model (dashed and dash-dotted); (c) using a free-electron model parabolic fit (dashed); and (d) using the screened-atomic model (dashed). Theoretical calculations have been convoluted with a Gaussian of width σ = 0.4 a.u. Experimental data are plotted with 1σ error bars.

This study addresses questions identified in previous studies by Alexandropoulos et al. on the screened-atomic model with effective charge Z = 1 was shown to fail in describing the experimental spectrum. The model with Z < 1 proved worse in predicting the difference Compton
profile. However, a screened model a with Z = 1.6 as well as a model in which the electron of the hydrogen was assumed to occupy the electronic band of Bakalis et al.\textsuperscript{5} yielded better agreement with experiment. Here, we show that state-of-the-art DFT-based calculations of Compton profiles of Ti and TiH\textsubscript{2} provide an excellent description of the measured difference Compton profiles without invoking any free parameters.

Our experimental approach is robust across measurement by two very different detectors – a Hitachi Vortex SDD and a high-resolution superconducting TES. It also offers possibilities for exploiting the Compton scattering techniques by using the readily accessible hard X-ray regime (below 30 keV) at low-flux synchrotron bending magnet beamlines. Finally, our study indicates the value of developing a tabletop Compton spectrometer as a laboratory-based spectroscopic tool for investigating electronic structures of materials. Existing portable X-ray fluorescence spectroscopy techniques make use of the intensity of the Compton peak to determine light-element content in the sample, including for calibration, e.g. Fig. 3 in of Laperche and Lemière\textsuperscript{26}. Our work demonstrates that in Compton profiles with similar incident energies and resolutions, information about electronic structure is also available. We also find focusing on difference profiles greatly reduces the complexity of analysis and experimental data corrections needed, again improving accessibility. This advancement holds promise for a wide range of applications\textsuperscript{17} in materials science, environmental analysis, biomedical research, among other areas.

![FIG. 5. Difference profile $A(p_z)$ (TiH\textsubscript{2} - Ti) measured with a superconducting Transition-Edge Sensor array (solid, in all plots), compared with the corresponding calculations (a) using the DFT methods of this paper (dashed); (b) using two possible electronic configurations of TiH\textsubscript{2} (see main text), and the free-atom Hartree-Fock model (dashed and dash-dotted); (c) using a free-electron model parabolic fit (dashed); and (d) using the screened-atomic model (dashed). Theoretical calculations have been convoluted with a Gaussian of width $\sigma = 0.19$ a.u. Experimental data are plotted with 1σ error bars, every 3 points for clarity.](image)

### Supplementary Material

The supplementary material provides further experimental and computational details, including X-ray diffraction patterns, asymmetry of Compton profiles, analysis of the density of states, charge density distribution, Bader charge analysis, and convergence testsings.

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### Data Availability Statement

The data that support the findings of this study are available from the corresponding authors upon reasonable request.


