

On the use of Fourier-transformed Compton profile for the determination of band occupancies in certain solids

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Abstract. The Pattison-Williams method of using Fourier-transformed Compton profiles for obtaining Fermi momenta in simple metals, is extended to set up a scheme for inferring d or f band occupancies in transition metals, rare earths etc. CP measurements are reported for Ni, α -Mn and β -Mn and then the new scheme is applied to obtain $3d$ occupancies in these systems. Some comments on the use of this method for other systems are also made.

Keywords. Compton profile; Fourier-transformed Compton profile; d -band occupancy.

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1. Introduction

Fourier-transformed Compton profile (FTCP) has been used to evaluate the Fermi momenta (p_F) of 'simple metals' (Pattison and Williams 1976). The method basically exploits the fact that the conduction electrons (n in number) in a simple metal may be treated as a free electron gas, and the FTCP for such a system is given by

$$B(r) = \frac{3n}{p_F^2 r^2} \left[\frac{\sin(p_F r)}{p_F r} - \cos(p_F r) \right]. \quad (1)$$

The zeros (r_0) of $B(r)$ occur at fixed values of the dimensionless quantity $p_F r$ viz 4.4934, 7.7253, 10.9041 etc. p_F can then be estimated from experimentally determined positions of the zeros. Thus Compton scattering experiment on a polycrystalline (isotropic) sample leads to an average p_F . Later Das and Chaddah (1983) pointed out that the Pattison-William scheme needs to be modified to include electron-electron correlation effects, and suggested a simple prescription for estimating the shift in the location of zeros when correlations are taken into account. In this paper we shall treat the conduction electrons as a homogeneous interacting electron gas *à la* Das and Chaddah instead of a free electron gas. A major advantage of p_F determination using FTCP is that this approach is applicable even in impure metals or disordered alloy samples, where the electron mean free path is small and so the usual Fermi surface (FS) measurement techniques (e.g. de Haas-van Alphen (dHvA) effect, cyclotron resonance etc) are not applicable.

To our knowledge, so far the above method has been employed only for simple (free electron-like) metals such as Na, Li, Al etc. However, in this paper we point out an obvious extension of the Pattison-William scheme that can be used for the determination of occupancies of different bands in certain solids. This extension can, in

principle, be applied to transition metals and such other systems (say, rare earths) that involve a coexistence of localized as well as delocalized electrons; the latter displaying a CP behaviour similar to that shown by the valence electrons in simple metals and the former showing features akin to those shown by the atomic state electrons. The feasibility of separating the two types of electrons—whose energies are otherwise very similar—comes about because the momentum distribution of the delocalized electrons may be pictured as that from a modified free electron gas giving a contribution to FTCP similar to (1). A practical scheme to achieve this separation will be presented here. A brief account of this work has been presented before (Das and Sahni 1986). The plan of the paper is as follows. In §2 we develop the method with specific reference to 3d transition elements and illustrate its actual usage with examples in §3. A critique of the method is presented in §4.

2. Method

CP gives a measure of the momentum distribution of all the electrons. Separation of core and valence electron contributions in momentum space is sometimes difficult. On Fourier transformation, however, we get the position space quantity $B(r)$ in which the two contributions can be separated easily. In the context of positron annihilation angular correlation studies, Gupta and Siegel (1979) had actually shown how the core contribution to the momentum spectrum, when projected in real space remains localized to $r < 2$ a.u. This argument is equally valid in the case of CP. The core electron contribution is important only in a very restricted region of r -space (r close to zero) while for $r \gtrsim r_0$ (the first zero of $B(r)$) i.e. in the oscillating region of $B(r)$, the contribution comes mostly from the valence electrons. In a typical transition metal there are both s and d electrons in the valence band. The s -electrons can be described reasonably well in terms of plane waves, albeit modified due to correlations. The presence of d -electrons, because of their partially localized nature, in general affects the positions of the zeros of the experimental $B(r)$. However, if only the s -electron CP can be separated out, one can obtain p_F using zeros of its FT. Then using the relation $\Omega p_F^3 = 3\pi^2 n_s$, we can calculate n_s , the number of s -electrons and hence the d -band occupancy. To exploit this recipe, we should make sure that the contributions coming from the core and d -electrons are properly subtracted from the experimental data. How this may be done in a consistent way is discussed below.

The easiest way to simulate the partially localized behaviour of the d -electrons, is to start with the free atomic wave function, truncate it at the Wigner–Seitz boundary and renormalize it. Such a renormalized free atom (RFA) approach reproduces the experimental isotropic CP's of transition metals tolerably well (Paakkari *et al* 1974). In our present method, we shall therefore adopt this RFA model to estimate the d -electron CP. Let us take a typical 3d transition metal with a total of $N = Z - 18$ electrons outside the argon core (here Z is the atomic number). If n_s denotes the number of s -electrons, then $n_d = N - n_s$ is the d -band occupancy (in the metallic state). In order to determine n_s (and hence n_d) in a consistent way, from the experimental CP, we go through the following steps.

First, we subtract from the raw CP data, the contributions due to multiple scattering

and the innermost core electrons which do not obey impulse approximation (usually only the 1s electrons for 3d metals). After deconvoluting the single scattering contribution, the data are converted from photon energy to electron momentum scale. Thus the final CP $J_{\text{exp}}(q)$ is produced (high and low energy side separately) from $-q_{\text{max}}$ to $+q_{\text{max}}$ with a mesh size say Δq .

Now the contribution to the above CP from core electrons (2s through 3p) viz $J_c(q)$ can be obtained from the tabulation of Biggs *et al* (1974) over the same q range viz $(-q_{\text{max}}, +q_{\text{max}})$. Let A_c be the area of this $J_c(q)$ within $\pm q_{\text{max}}$. Similarly, we may calculate the RFA-CP $J_d(q)$ of a d -band electron; and find its area A_d within $\pm q_{\text{max}}$.

Evidently we must normalize $J_{\text{exp}}(q)$ over $(-q_{\text{max}}, +q_{\text{max}})$ to an effective number of electrons (contributing to the profile), given by,

$$A = A_c + (n_d \cdot A_d) + n_s. \quad (2)$$

Of course, implicit in (2) is the assumption that the profile of 4s electrons lies well within $\pm q_{\text{max}}$. We next calculate

$$J_s(q) = J_{\text{exp}}(q) - [J_c(q) + n_d J_d(q)]. \quad (3)$$

As we shall see, $J_s(q)$ may show oscillations in the tail region. Although a priori one might expect that there can be two sources of these (i) due to use of RFA approximation, instead of a more accurate band structure calculation and (ii) because of the statistical error in $J_{\text{exp}}(q)$, we have confirmed from actual calculation that use of RFA predominantly affects the low q values of CP. So these oscillations are largely due to (ii). A way to get rid of the unphysical oscillations in the tail is the following. Since $J_s(q)$ represents the residual profile contributed solely by the 4s electrons, it should be confined to low q region. We therefore fit $J_s(q)$ to a parabola plus a 'correlation tail' (Das and Chaddah 1983), keeping the peak height unchanged and preserving the area (n_s) under it. Let us call the fitted curve as $\tilde{J}_s(q)$.

Finally, we numerically evaluate the FT of $\tilde{J}_s(q)$ to get $B(r)$. Once p_F is estimated from its first zero, we can get the number of free electrons \bar{n}_s via

$$\Omega p_F^3 = 3\pi^2 \bar{n}_s. \quad (4)$$

In a practical calculation we proceed as follows. We assume initially a value for n_s and go through all the steps upto equation (4) to arrive at \bar{n}_s . We iterate until the starting number n_s matches with the number \bar{n}_s obtained from (4). The n_d thus obtained should be the correct (self-consistent) value for the d -band occupancy in the metallic state. Of course, the filled shell core contribution and the RFA based 3d profile should both be convoluted with the residual instrumental function (RIF) (Paattero *et al* 1974) before they are subtracted from the deconvoluted experimental profile. Strictly speaking since RFA wave functions themselves depend on the occupancy of d -band, in each iteration, as the d -band occupancy is changed we should permit corresponding changes in the d -state CP contribution. However, for this, one would have to start with different Clementi wave functions at each step of the iteration and that makes the calculations cumbersome. But fortunately, for a first order estimate we can neglect this variation as it is expected to introduce only a second order correction. We shall now test the validity of the above mentioned ideas by taking two typical transition metals viz Ni and Mn.

3. Experimental verification

The Compton spectrometer used for measurement of CP's consists of (i) a 100 mCi ^{241}Am disc source emitting 59.54 keV γ -rays; (ii) a high purity planar Ge detector with an active diameter of 10 mm and a sensitive depth of 7 mm; (iii) a 1 K MCA. The sample chamber is designed such that the mean scattering angle is 165° . The detector-preamplifier combination is coupled to a spectroscopy amplifier having usual facilities for base line restoration, pulse pile-up rejection etc. The channel slope is usually kept near 40 eV/ch for convenience of calibration. In the Compton peak region (~ 48.5 keV), the resolution of our detector-electronic combination, measured using a $10\ \mu\text{Ci } ^{210}\text{Pb}$ source (γ -energy 46.55 keV) turns out to be 320 eV (FWHM). Taking into account the 'geometric resolution' due to finite beam collimation, the total instrumental resolution is estimated to be 340 eV or 0.55 a.u. in momentum space (Das 1985).

Isotropic CP's (ICP) of 99.99% pure Ni as well as α and β phases of Mn were measured and we present our results for these metals one after the other. Our experimental CP of Ni agrees well with the previous result (Paakkari *et al* 1975). $J_d(q)$ was calculated from the RFA model (Bergren 1972) starting with the Clementi wave function (Clementi and Roetti 1974) in $3d^9 4s^1$ configuration ignoring any changes in RFA wave functions for the neighbouring configurations. The procedure outlined in §2 was then carried out by varying the parameter n_s between 0.5 and 2.0; for each value of n_s we obtained a $J_s(q)$ and its corresponding fitted curve $\bar{J}_s(q)$. Figure 1 shows the superposition of these two curves for $n_s = 1.00, 1.34$ and 1.50 . Fourier transforms of $\bar{J}_s(q)$ yields $B(r)$. Figure 2 shows how the zeros for $B(r)$ shift to higher values as n_s decreases. Finally we plot (figure 3) both n_s and \bar{n}_s as a function of n_d . The cross-over point gives the self-consistent value $n_s = \bar{n}_s = 1.34$, which means $n_d = 8.66$.

At this stage we would like to comment on the possible error in the estimated n_s values. Because of the statistical uncertainty in the experimental counts, there is a finite error bar for each $J_{\text{exp}}(q)$. Since it is difficult to calculate how the actual error in $J_{\text{exp}}(q)$ propagates through to n_s , we estimate an upper bound of error on n_s using a more straightforward approach. Starting from the random error in the counts in each channel one can show (Das 1985) that the standard deviation in experimental CP is

$$\sigma [J_{\text{exp}}(q)] = \sqrt{[N_e J_{\text{exp}}(q)] / [N_{\text{tot}} \Delta q]}, \quad (5)$$

where N_e is the total number of electrons within $\pm q_{\text{max}}$ and N_{tot} is the total number of counts in all the channels. Using our experimental values of $N_e \approx 22.5$, $N_{\text{tot}} \approx 2 \times 10^6$, $\Delta q = 0.05$ a.u. one can estimate $\sigma [J_{\text{exp}}(q)]$ at each q -value. If one then generates the two extremum profiles $J_{\text{exp}}(q) \pm \sigma [J_{\text{exp}}(q)]$ and follows the self-consistent procedure, described above, in each case separately, one obtains the two bounds of n_s values as 1.30 and 1.38. Consequently, the upper bound of error on $n_s = 1.34$, due to statistical uncertainty in counts is ± 0.04 i.e. $\sim \pm 3\%$.

Next we come to manganese, which is the only 3d transition metal for which no electronic charge or momentum density studies had been done (Weiss and Mazonne 1981). Amongst the four known allotropic modifications of Mn (Sully 1955) only α -Mn and β -Mn can be obtained in stable condition at room temperature and ours was the first measurement for these two phases (Das and Sahni 1984). The β -phase polycrystalline sample was prepared by heating α -Mn to $\sim 900^\circ\text{C}$ for about an hour and then rapidly quenching it across $\alpha \rightarrow \beta$ transition temperature (725°C). Structures and

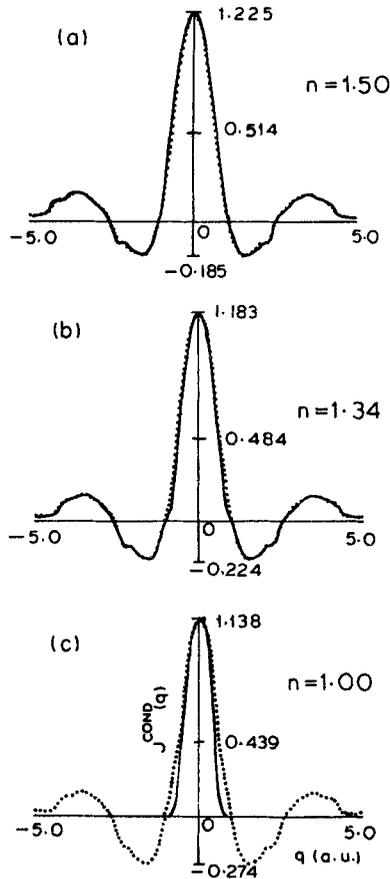


Figure 1. The conduction electron profiles (dotted curves) $J_{\text{cond}}(q)$ for (a) $n = 1.50$, (b) $n = 1.34$, (c) $n = 1.00$ are shown. The continuous curves are the fitted parabola with 'correlation tails'.

single phase characters of the samples were confirmed by x-ray powder diffraction studies. Around 20,000 counts per channel were accumulated in the Compton peak for both the 1 mm thick α -Mn and the 1.5 mm thick β -Mn sample. The deconvoluted CP's $J^{\alpha}(q)$ and $J^{\beta}(q)$ were normalized to 20.56 electrons between $\pm q_{\text{max}}$ (we have taken $q_{\text{max}} = 5$ a.u.). Figure 4 shows the deconvoluted profiles, where one can see that $J^{\beta}(0)$ is only $\sim 2\%$ higher than $J^{\alpha}(0)$. Starting with Clementi wave functions corresponding to $3d^6 4s^1$ configuration, the d -band occupancies are then calculated in an exactly similar fashion as was done in the case of Ni. Figure 5 shows the subtracted $4s$ profiles $J_s(q)$ for α and β phases superposed; the difference between the two phases is much more prominent here as compared to that in figure 4 where the complete profiles are shown. The best fitted parabola to these conduction electron profiles are then Fourier transformed. The Fourier transforms $B(r)$ for both α -Mn and β -Mn are plotted in figure 6, which clearly shows the shift in the zeros. Finally figure 7 shows the two crossing points of \bar{n}_s^{α} vs n_d and \bar{n}_s^{β} vs n_d curves with the n_s vs n_d straight line giving the self-consistent values of n_s as 0.93 for α -Mn and 1.12 for β -Mn. The d -band occupancy thus decreases from 6.07 to 5.88 as we go from α -Mn to β -Mn.

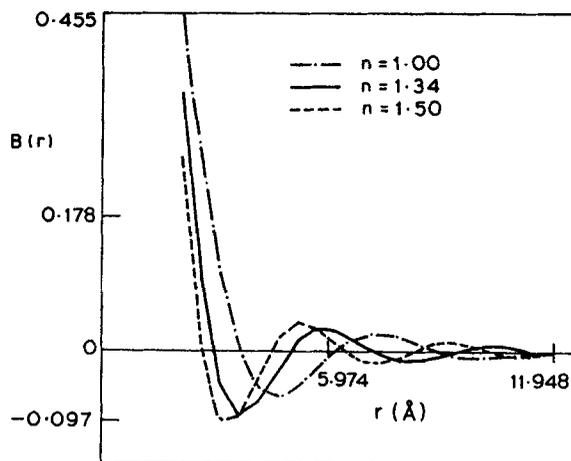


Figure 2. $B(r)$, the Fourier transform of the conduction electron CP $J_s(q)$ for different numbers of conduction electrons viz $n_s = 1.00, 1.34, 1.50$. The zeros shift to a lower value as n_s increases.

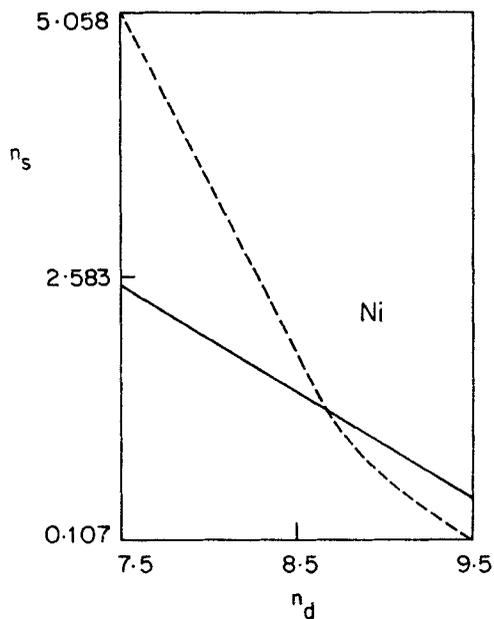


Figure 3. Number of conduction electrons (\bar{n}_s) obtained from the first zero of the $B(r)$, is plotted as a function of n_d , the starting number of d electrons. This dashed curve crosses the n_s vs n_d straight line at a fixed point, which corresponds to the self-consistent value $n_s = 1.34$.

4. Discussion

In this paper we have outlined a method for estimating d -band occupancies in transition metals using FTCP. Our method is based on the assumption that there is

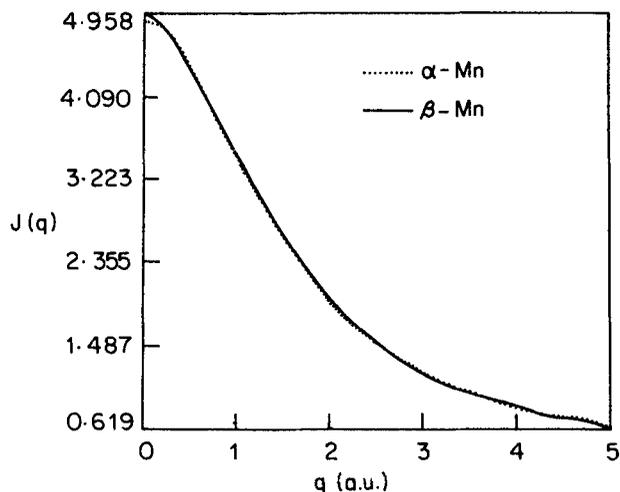


Figure 4. Deconvoluted experimental CP's of α -Mn, $J^{\alpha}(q)$ (.....) and β -Mn, $J^{\beta}(q)$ (——).

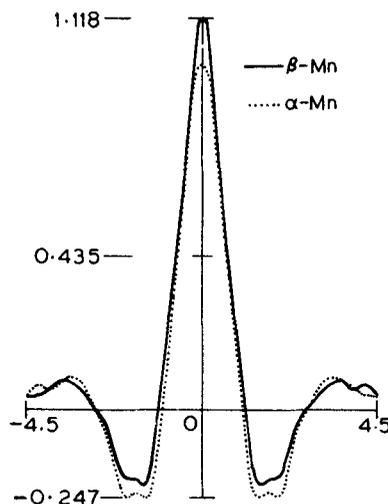


Figure 5. Comparison of the conduction electron CP's $J_c(q)$ of α -Mn (.....) and β -Mn (——).

little s - d admixture (hybridization) and that RFA model gives a good description of the d -electrons. We have applied our scheme to two transition metals Ni and Mn. The result $n_d = 8.66$ for Ni obtained by us is in close agreement with what Paakkari *et al* (1975) deduced from their experimental CP data on Ni using the RFA model. We believe that, for the α and β allotropes of Mn, the difference in their d -band occupancies deduced by us should be discernable in a careful x-ray or ultraviolet photoelectron spectroscopy study. Such a measurement should be carried out to test the viability of our scheme.

The above technique of determining the d -band occupancy in a self-consistent way, can not only be used for other transition metals, rare earths etc., but also employed to

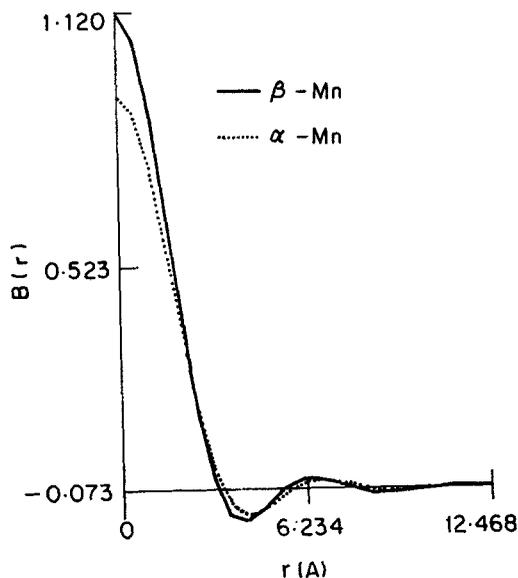


Figure 6. Fourier transforms $B(r)$ for α -Mn and β -Mn for $n_s = 0.93$ and $n_s = 1.12$ respectively. The shifts in the zeros are clearly visible.

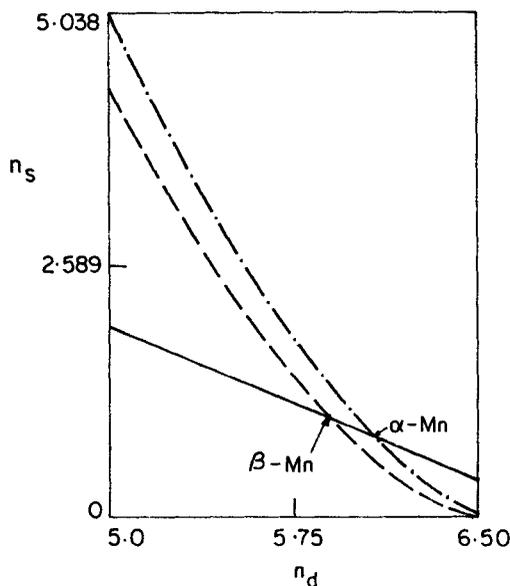


Figure 7. Number of conduction electrons (\bar{n}_s), obtained from the first zero of $B(r)$, is plotted as a function of n_d ; (a) α -Mn and (b) β -Mn. These curves (---) cross the n_s vs n_d straight line at two fixed points, which correspond to the self-consistent values of n_s , viz 0.93 for α -Mn and 1.12 for β -Mn.

get the amount of charge transfer in alloys like nickel-aluminium. Moreover, this prescription affords a way to explore the systematic trends in the d - or f -band occupancies in different transition element series. It is worthwhile attempting such an extension based on the use of FTCP and we hope to do it in the near future.

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