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Compton profile study of α-manganese

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Abstract. The results of a Compton profile study on polycrystalline α-Mn are reported. Our measuremei are compared with theoretical results computed for different $3d$-$4s$ electron configurations within the RFA model. Best agreement between the measured and calculated values is found for $3d^{5\cdot4}4s^{1\cdot6}$ configuration. Theoretical Compton profile of γ-Mn calculated using the same procedure is close to that for bcc phase with similar electron configurations.

Keywords. Compton scattering; electron momentum distribution; electron states; renormalized-free-atom model; band structure; Compton profile.

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1. Introduction

Mn belongs to the $3d$ group of transition metals and exists in many allotropic forms, most of which have complicated structures (see, for example, Pearson 1964). α-Mn, stable at room temperature, has a complicated A12 type bcc structure ($a = 8{\cdot}90$ Å) with 58 atoms in the conventional unit cell. The other forms β, γ and δ are stable at various temperatures between 742°C and the melting point (1244°). As pointed out by several workers (see, for example, Cracknell 1971) the computation of the band structure and the Fermi surface of α-Mn is almost an impossible task because of the large number of bands occupied by the valence electrons.

In the last decade Compton scattering has been recognized as a powerful tool to study electron structure in light and medium transition metals (Paakkari *et al* 1975; Berggren *et al* 1977; Sharma *et al* 1987, 1988 and references therein). In all cases studied with this technique, experimental results were predicted reasonably well at medium and high-momenta ($> 3{\cdot}0$ a.u.) by the free atom profiles. In the low momentum region more refined calculations employing both the band structure as well as simple renormalized free atom (RFA) models can explain the Compton line shapes. Among $3d$ metals, very little work has been reported on Mn. Gupta *et al* (1983) reported the first Compton profile measurement on polycrystalline Mn and observed that the measured values were much flatter than the convoluted free atom values at low momenta. Das and Sahni (1986) measured the Compton profile for α and β-Mn and determined the $4s$ band occupancies as 0·93 and 1·12 respectively. Their $J(0)$ values in α and β-phase differed by about 2% and were both $< 5\,e$/a.u. While a change of 2% in $J(0)$ is rather large, their $J(0)$ values are significantly lower than those observed for all other $3d$-metals and thus do not follow the trend of constancy pointed out by Gandhi and Singru (1981). Also their

values around 5 a.u. were much higher than the free atom values. It was therefore considered worthwhile to reinvestigate the case of Mn.

In this paper we present our experimental Compton profile for α-Mn corrected for various effects. In order to determine the 3*d*-4*s* configuration, theoretical Compton profile has been computed using the RFA model. Theoretical results for three different electron configurations namely $3d^64s^1$, $3d^{5\cdot4}4s^{1\cdot6}$ and $3d^54s^2$ are presented and compared with our experiment. Also, since theoretical results from band structure calculation on fcc (γ) Mn (Srivastava and Ojha 1984) were available, we extended our RFA calculations to fcc Mn also. These results described in detail elsewhere (Gupta 1987) have also been compared with those for α-Mn. In § 2 some salient features of our experimental method are discussed. Section 3 briefly deals with the method of calculation with the results and discussion in § 4.

2. Experimental procedure

The sample used in this study, a polycrystalline sheet of 2·67 mm (purity better than 99·9%), was prepared by vacuum sublimation method at the Uppsala University, Sweden. The details of the method are given elsewhere (Richardson 1981). Pure Mn ingot was placed in a recrystallized alumina crucible and covered with another similar crucible. The entire arrangement was placed in an evacuated chamber of an RF furnace heated to about 1100°C. The greyish white and brittle sample so obtained was subjected to X-ray diffraction analysis at USIC, Roorkee, employing an X-ray generator (PW1140/09) having a Zr filter with Mo target (35 kV, 20 mA). The diffraction patterns confirmed the sample to be α-Mn with lattice constant (*a*) in agreement with the value accepted for this phase (Pearson 1964).

The Compton profile has been measured using the high intensity Compton spectrometer described elsewhere (Singh 1986; Das Gupta *et al* 1988; Sharma *et al* 1988). The experimental procedure is briefly summarized in what follows: Gamma-rays from a 5 Ci annular ^{241}Am source were scattered by the sample (α-Mn) through a mean angle of 160° (± 2·5°) and detected using a planar intrinsic Ge detector (FWHM 415 eV at 60 keV). The channel width (58·6 eV) corresponds to < 0·1 a.u. of momentum. About 65,000 counts/channel were collected at the Compton peak in 18,000 seconds A separate measurement was made without the sample to obtain the background contribution which was scaled to the measurement time for the sample and then subtracted point by point from the measured data. The Compton peak-to-background ratio was about 600:1. After background subtraction the profile was corrected for the effects of instrumental resolution, sample absorption and energy dependence of the Compton scattering cross-section and then converted to the momentum scale to obtain $J(p_z)$ (Manninen *et al* 1974; Paatero *et al* 1974). Since the sample thickness was not negligibly small, the multiple scattering was corrected following the Monte Carlo procedure of Halonen *et al* (1975). This removed the contribution of elastic and inelastic double scattering (DS) events. The effect of DS correction at $J(0)$ was about 4·8%. Finally, the experimental Compton profile was normalized to have an area of 11·07 electrons which corresponds to the area of the free atom profile in 0–7·0 a.u. The contribution of 1*s* electrons was included only upto 6 a.u. because in our arrangement for higher p_z values the recoil energy becomes less than the K-shell binding energy in Mn.

3. Calculation

Following Berggren (1972), the Compton profile $J(p_z)$ for a polycrystal measured along the p_z direction is related to the electron momentum density $\rho(\mathbf{p})$ through the equation

$$J(p_z) = \int_{p_z}^{\infty} 2\pi \langle \rho(\mathbf{p}) \rangle p \, dp, \tag{1}$$

where $\langle \rho(\mathbf{p}) \rangle$ is the spherical average of the electron momentum density $\rho(\mathbf{p})$ and integration is over the plane of constant p_z.

In order to calculate $J(p_z)$ one must know $\rho(\mathbf{p})$. For the inner core electrons free atom wavefunctions can be used and then it is straightforward to obtain $\rho(\mathbf{p})$ for these electrons. For valence electrons, as pointed out earlier, the band structure methods cannot be applied in the present case because there are more than 100 occupied bands in α-Mn (Cracknell 1971). We, therefore, followed Berggren's (1972) approach based on the RFA model which is known to be a reasonable compromise between the crude free atom model and the elaborate band structure methods. It was noticed that using the RFA model Gelatt *et al* (1977) had computed the cohesive energy for Mn choosing an fcc structure and their value was in close agreement with the measured data. As is well known, in this approach the free atom wavefunctions are truncated at the Wigner-Seitz (WS) sphere and renormalized to unity within the WS sphere to preserve charge neutrality. Thus, the first problem was the choice of the WS radius because in α-Mn the arrangement of atoms in the 58-atoms unit cell is complex with three different types of atoms having a different volume for each state. In order to overcome this situation we assumed that the total energy (also the cohesive energy) is sensitive to the density but is only weakly dependent on the crystal structure (see, for example, Gelatt *et al* 1977; Min *et al* 1986). Since the total energy is directly related to the second moment of Compton profile, it is natural to expect that the 'spherically-averaged' Compton profiles would also exhibit little sensitivity to the crystal structure as has been observed by several workers (see, for example, Bacalis *et al* 1986; Ahuja *et al* 1987). We, therefore, first determined the average volume per atom of the unit cell of α-Mn and then the value of WS radius. This procedure ensured that the bulk density in the simple structure (bcc) remained the same. In this way we expected to obtain a reasonable estimate of the 'averaged' Compton profile for the valence electrons in α-Mn. The value of WS radius so obtained was 2·7 a.u. It turned out that about 30% of the 4s wavefunction was in the WS sphere compared to a value of 95% in the $3d$ electrons. The effect of the renormalization was therefore considered only for $4s$ electrons. In figure 1 we plot the free atom as well as RFA wavefunctions for $4s$ electron for $3d^5 4s^2$ configuration.

For cubic metals, the Compton profile $J_{4s}(p_z)$ for $4s$ electrons can be written as (Berggren 1972)

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

where $\mathbf{K}_n$ is a reciprocal lattice vector and p_z the projection of electron momentum $\mathbf{p}$ along the scattering vector direction. $\psi_0^c(\mathbf{K}_n)$ is the Fourier transform of the RFA wavefunction. $G_n(p_z)$ is the auxiliary function involving reciprocal lattice vectors K_n and the Fermi momentum p_F as discussed by Berggren (1972). The Compton profile $J_{4s}(p_z)$ was computed for the bcc structure from equation(2) for different $3d$-$4s$ configurations.

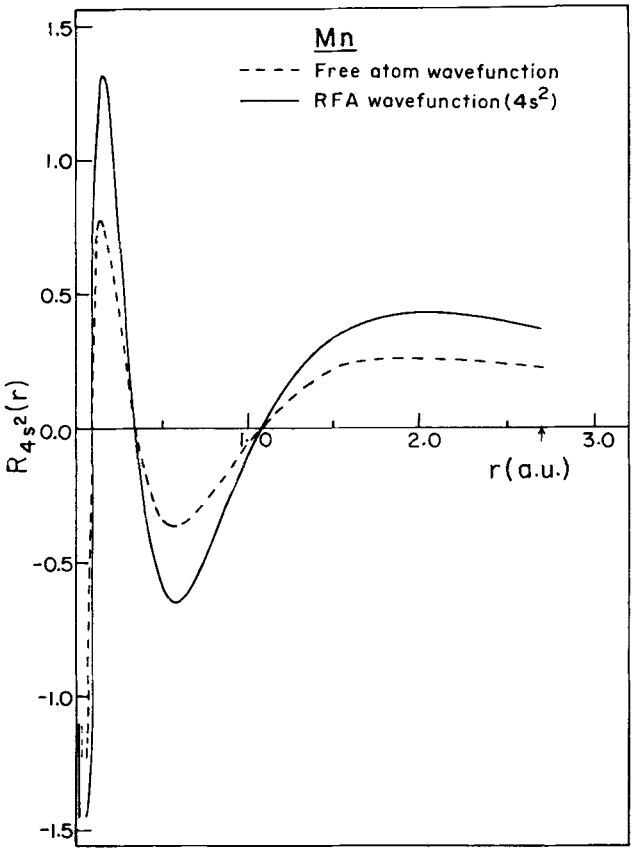

Figure 1. Free atom 4*s* wavefunction (for Mn) before (----) and after (—) truncation and renormalization to one within the Wigner-Seitz sphere.

The free-atom Hartree-Fock wavefunction for Mn was taken from Clementi and Roetti (1974) for $3d^6 4s^1$ and $3d^5 4s^2$ configurations. For the configuration $3d^{5\cdot4}4s^{1\cdot6}$, the wavefunction for the $3d^5 4s^2$ was used but the value of p_F and the normalization of $J_{4s}(p_z)$ was kept according to the number of 4*s* electrons (i.e. 1·6). The values of the Compton profile of 3*d* electrons and other inner electrons were taken from Weiss *et al* (1968). The total theoretical Compton profiles corresponding to all electrons in α-Mn were obtained for the above three configurations by adding these contributions and then convoluted with the residual instrumental function (RIF) for a proper comparison with the deconvoluted experimental data (Paatero *et al* 1974).

4. Results and discussion

The experimental Compton profile for α-Mn is presented in table 1 along with our results of RFA calculations for three configurations namely $3d^6 4s^1$, $3d^5 4s^2$ and $3d^{5\cdot4}4s^{1\cdot6}$. Theoretical values have been convoluted with the RIF of our spectrometer (Singh 1986) and all these values are also normalized to 11·07 electrons. The

Table 1. Theoretical and experimental Compton profiles of polycrystalline α-Mn.

p_z (a.u.)	Theory (RFA) Core + $3d^64s^1$	Core + $3d^54s^2$	Core + $3d^{5\cdot4}4s^{1\cdot6}$	Experiment Before D.S.	After D.S.
0·0	5·113	5·463	5·340	5·034	5·276 ± ·037
0·1	5·080	5·435	5·306	5·030	5·256
0·2	5·009	5·365	5·231	4·985	5·190
0·3	4·879	5·232	5·091	4·899	5·069
0·4	4·731	5·063	4·919	4·776	4·921
0·5	4·541	4·830	4·696	4·620	4·749
0·6	4·362	4·587	4·463	4·438	4·547
0·7	4·159	4·299	4·211	4·238	4·338
0·8	3·985	4·042	3·978	4·028	4·118
0·9	3·801	3·774	3·756	3·816	3·893
1·0	3·644	3·559	3·566	3·605	3·664 ± ·031
1·2	3·334	3·196	2·246	3·209	3·224
1·4	3·028	2·908	2·962	2·855	2·844
1·6	2·714	2·621	2·659	2·539	2·520
1·8	2·402	2·315	2·342	2·250	2·222
2·0	2·111	2·023	2·051	1·988	1·946
2·5	1·532	1·477	1·507	1·476	1·426
3·0	1·131	1·101	1·120	1·128	1·084
3·5	0·876	0·854	0·871	0·887	0·851
4·0	0·715	0·706	0·710	0·734	0·704
5·0	0·464	0·450	0·452	0·533	0·516 ± ·011
6·0	0·335	0·317	0·333	0·395	0·381
7·0	0·249	0·247	0·247	0·283	0·274

experimental results before and after double scattering (DS) correction are also given in table 1. It is seen that the DS correction sharpens the Compton profile and increases the value at $p_z = 0$ by about 4% which is not unexpected in view of the fact that our sample was 2·7 mm thick.

A comparison of the various theoretical values given in table 1 shows that in the low momentum region the RFA values for $3d^54s^2$ and $3d^{5\cdot4}4s^{1\cdot6}$ are higher than the experimental values but those for $3d^64s^1$ are smaller. Between 0·6 and 1·0 a.u. the trends get reversed and the experimental values are somewhat larger than the theoretical values. In the high momentum region all theoretical values are nearly the same (due to the same core) and are all close to the experiment. In Mn, the impulse approximation can be considered valid for all except the 1*s* electrons. However, it turns out that the contribution of 1*s* electrons is very flat and at $p_z = 0{\cdot}0$ it is only 0·0348 e/a.u. which is less than 1% of the total $J(0)$ value and our experimental errors are also of this magnitude. Although there would be some effects of non-validity of IA, in view of the above this is not expected to alter significantly the analysis of the data in the low momentum region. In the region of high momenta, the agreement between theory and experiment is already quite good and within 0·06 to 0·01. This point was discussed in our earlier paper on Co (Ahuja *et al* 1987) and we refer the reader to this. We shall, however, like to mention the example of polycrystalline Ni for which excellent agreement was found in

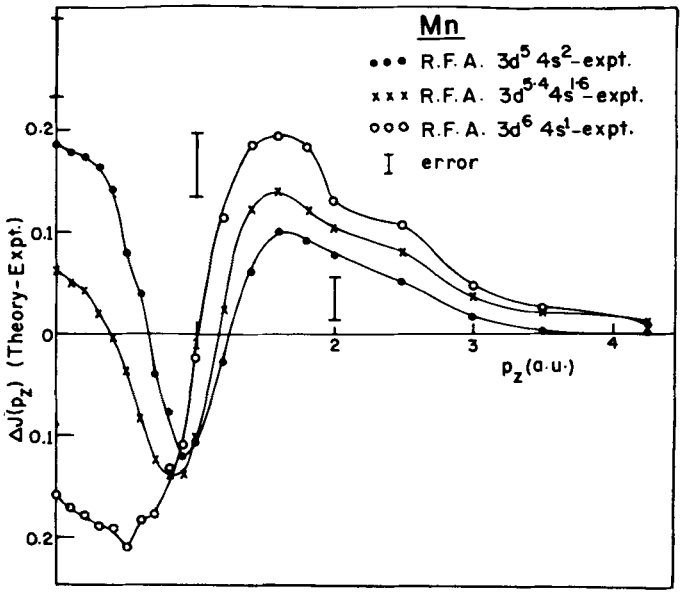

Figure 2. Difference ΔJ profiles for polycrystalline α-Mn. The theory has been convoluted with the residual instrumental function.

the Compton profiles (better than 0·5%) measured with 60 and 412 keV gamma rays (Manninen *et al* 1981 and Rollason *et al* 1987).

In figure 2 we plot the difference between theory and experiment for the various calculations. It is seen that for $3d^{5\cdot4}4s^{1\cdot6}$ configuration not only the difference in $J(0)$ is small but even the overall deviations are small. In fact, we calculated $\sum_{p_z=0}^{7}|\Delta J(p_z)|^2$ for all configurations and found it to be the lowest for this case. Thus this analysis suggests that $3d^{5\cdot4}4s^{1\cdot6(\pm0\cdot1)}$ configuration is in better agreement with the experiment compared to other configurations and thus the $3d$ band occupancy from our work comes out to be $5\cdot4 \pm 1$. This estimate of d band occupacy is in good agreement with the value of Snow and Water (1969) for Mn obtained from an APW computation. It is, however, somewhat lower than the value of Das and Sahni (1986). It may be mentioned here that Gandhi and Singru (1981) have calculated the Compton profiles for a number of $3d$ metals (except Mn) using the RFA model for different $3d$-$4s$ electron configurations. Their results showed that the $J(0)$ values were almost the same in all $3d$ metals for a particular configuration. This constancy in $J(0)$ had also been observed in the experimental data (Weiss 1973; Manninen and Paakkari 1974). Interestingly our $J(0)$ value for α-Mn ($5\cdot276 \pm 0\cdot037$) also lies in the range of values observed experimentally for other $3d$ metals. This seems somewhat surprising because Mn shows a distinct behaviour than its neighbours (Cr, Fe) which are both bcc metals with much larger cohesive energies. This closeness in $J(0)$ values might be accidental also as the origin of constancy in $J(0)$ still remains to be understood. However, Das and Sahni (1986) measured the $J(0)$ value for α-Mn considerably lower than our $J(0)$ value (5·27). Their value for $p_z = 5\cdot0$ a.u. is 0·6 whereas our value is $0\cdot516 \pm 0\cdot011$ and the theoretical value is only 0·45. It looks that their other values for $p_z > 5\cdot0$ a.u. may also be larger than ours.

As a consequence of normalization their low momentum values could be lower and hence the difference, Their large value in the high momentum region is probably due to improper DS correction and also instrumental resolution.

Next we consider the case of γ-Mn which has been investigated theoretically using the band structure method by Srivastava and Ojha (1984). We extended the RFA calculations to this phase also and considered two values of lattice constants (a) because the value of a used by Srivastava and Ojha was 6·543 a.u. which is substantially smaller than 7·269 a.u. generally accepted for this phase (Pearson 1964). These results have been discussed in detail elsewhere (Gupta 1987) and hence we make only some general comments. It was observed that the values of Compton profiles calculated for fcc Mn with $a = 7{\cdot}269$ a.u., were nearly equal to those for bcc Mn discussed earlier when the same configuration was considered. This is in agreement with the earlier observation that Compton profiles show little sensitivity to crystal structure. It was also noticed that the RFA values were flatter than the band structure results and the effect of reducing a was to flatten the profile in the low momentum region. Unfortunately no experimental results are available for examining more closely the results on fcc Mn. However, this comparison suggests that the Compton profiles for α and γ phases as obtained in the RFA model with so different crystal structures are almost the same. In the case of cobalt, Ahuja *et al* (1987) have found that $J(p_z)$ values for hcp and fcc phases for $3d^7 4s^2$ cases were nearly the same. Thus a change of 2% observed in $J(0)$ by Das and Sahni (1986) between α and β phase of Mn is rather surprising and calls for further investigation. The number of holes in $3d$ band can also be determined from EELS (electron-energy-loss spectrum) and L-edge XANES (X-ray absorption near-edge structure) studies but the analysis has to be done carefully.

5. Conclusion

In this paper we have presented experimental Compton profile for polycrystalline α-Mn and compared this with theoretical results for different outer electron configuration within the RFA model. It is shown that the RFA model provides a good overall description of the total and valence electron profile. The most favoured electron configuration for α-Mn is found to be $3d^{5{\cdot}4}4s^{1{\cdot}6}$ in agreement with estimates of Show and Waber. This work highlights the efficacy of Compton scattering studies in metals having a complex structure. More measurements with other established techniques such as EELS, XANES can be expected to help in providing a clearer understanding of the electronic structure of Mn.

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