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Electron momentum density distribution in iridium by Compton scattering technique

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Abstract. The isotropic Compton profile of iridium, measured using 59·54 keV γ-rays, is reported in this paper. The results are compared with the theoretical Compton profiles from APW method with and without incorporating electron correlation effects. It is seen that correlation effects improve the agreement between the experiment and theory. Comparison with the renormalized-free-atom (RFA) model calculations has also been made. Behaviour of *d*-band electrons in Ir and some other 5*d* transition metals is discussed in terms of broadening in their Compton profiles.

Keywords. APW band structure calculation; Compton profiles; electron momentum density; electron–electron correlation effects; iridium.

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1. Introduction

Iridium (Ir), a transition metal of 5*d* group, has an fcc structure with lattice constant $a = 7{\cdot}225$ a.u. Since it is a heavy element, relativistic effects are expected to play an important role in describing the properties of this elemental solid. Considerable amount of work has been done to study this metal during the seventies. These include measurements of density of states, magnetoresistance, thermoelectric power, etc [1]. Traum and Smith [2] had performed relativistic band structure calculations to obtain density of states which were compared with the photoemission results [3]. Körling and Haglund [4] had reported electronic and cohesive properties of several transition metals using different approaches based on local density approximation. Using scalar relativistic augmented plane wave (SRAPW) method, Sigalas *et al* [5] had observed maximum occupancy in the valence bands of Co, Rh and Ir isogroup metals among all the transition metals. Mechanical properties of this metal had been studied by Adamesku *et al* [6]. Choy *et al* [7] had studied L_{III} edge of this metal in iridium oxide to investigate electronic configuration and covalency through XANES. As all platinum group metals are extensively used for catalytic purposes in chemistry, Kolaczkiewicz and Bauer [8] have studied the surface effects of these metals on W(110) surface at several temperatures using Auger electron spectroscopy. Recently, Chai *et al* [9] had done molecular activation analysis of Ir.

Compton scattering experiments are particularly sensitive to the momentum distribution of loosely bound valence electrons, and therefore provide an interesting way to probe the electronic structure of materials. Measurements of line shape on a polycrystalline sample yield the Compton profile, $J(p_z)$, which is the projection of electron momentum density along the direction of scattering vector. Within impulse approximation,

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

where $\langle \rho(\mathbf{p}) \rangle$ is the spherical average of electron momentum density $\rho(\mathbf{p})$. In our endeavour to make a systematic study of 5*d* transition metals, we have previously studied electron momentum density in Ta [10], W [11], Re [12], and Pt [13]. These studies on 5*d* transition metals have revealed interesting discrepancies between band structure theories and experiments. Papanicolaou *et al* [14] published theoretical Compton profiles along the three principal directions for several cubic transition metals including Ir. They have also reported isotropic Lam–Platzman correction term due to electron–electron correlation effects.

In this work we report on the first Compton profile study on polycrystalline Ir. To examine the systematics in the momentum distributions in 5*d* transition metals, a comparison of Compton profiles of 5*d* transition metals in terms of their fwhm and hence broadening due to varying 5*d* electrons has also been made. The paper is organized in the following way. First, we describe the experiment and various stages of data processing to extract the Compton profile. This is followed by a brief description of the method of theoretical calculations. In § 4 we discuss and compare our data with the available APW Compton profiles and our calculations based on RFA model. A comparison of Compton profiles of 5*d* transition metals studied so far by our group has also been made in terms of their full width at half maximum (fwhm).

2. Experiment and data analysis

Polycrystalline Ir sample used in this work was procured from M/s. Goodfellow Metals Ltd., UK. It was having 99·99% purity and 0·0125 cm thickness. The Compton spectrometer used in the measurement is the same as that reported earlier by Sharma *et al* [15]. γ-rays of 59·54 keV energy from a 5 Ci annular ^{241}Am source were Compton scattered at an angle of 165° ($\pm$ 2·5°). Due to the strong absorption in Am, the annular shape of the high activity ^{241}Am sources helps to spread the high activity onto a larger area while allowing the scattering angle constant. The Compton scattered γ-rays from the sample kept in vacuum of 10^{-2} torr were detected by a planar HPGe detector. The momentum resolution of the spectrometer which depends upon primary photon energy, angular divergence and the resolution of the detector, was about 0·57 a.u.. About 5×10^4 counts per channel (channel width $\sim$ 0·1 a.u.) were collected at the Compton peak in 43 h. The count rate at the Compton peak was $\sim$ 0·3 cps. The stability of the system was checked by using a weak ^{241}Am source, four times in a day during measurement.

The raw spectrum for Ir is shown in figure 1. The peak at channel number 742 is the main Compton peak. The sharp peak next to this is the elastic peak coming mainly

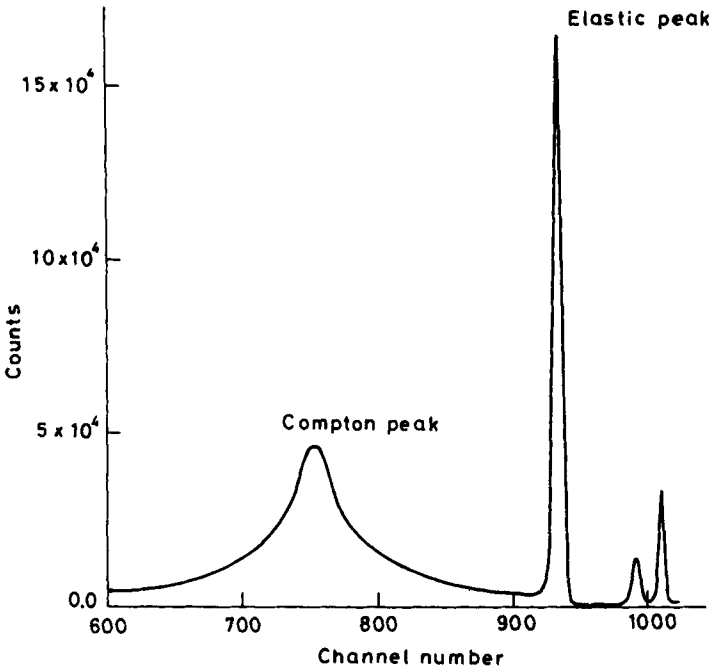

Figure 1. Energy distribution of photons from a ^{241}Am source scattered at 165° (± 2·5°) from a polycrystalline iridium. Each channel corresponds to 60 eV (see text).

from the electrons which are not contributing to the Compton profile. The contribution of the elastic peak in the high energy side of Compton profile was avoided by using a weak ^{241}Am source and the 'subtract' mode of our MCA. The third peak, from left, is the Ir $K_{\alpha 1}$, while the fourth peak corresponds to Ir $K_{\alpha 2}$. In our set-up the K-shell electrons are excited by the high energy gamma-radiation of ^{241}Am source. The measured background was subtracted from the raw Compton spectrum channel-wise after scaling it to the measuring time of the raw data. Thus the resulting spectrum was deconvoluted to take into account the insufficient charge collection by the detector at low energy side and the statistical noise in the experiment. Energy dependent corrections due to sample absorption and Compton cross-section etc. were made using the computer code of Perkkiö and Paakkari [16] and then the profile was converted into momentum scale. To find the effect of multiple scattering on Compton profile, a procedure based on Monte-Carlo method of Halonen *et al* [17] has been used. It was found that effect of double scattering is manifested in increase of the profile at $J(0)$ by 3·3% and decrease in high momentum region by about 2·6%. In the present experiment, the K-shell and L-shell electrons do not contribute to the Compton profile in momentum range of 0 to 7 a.u. as their binding energies [18] are more than the recoil energy ($\leqslant$ 11 keV). The experimental profile for Ir was, therefore, normalized to have an area of 26·67 electrons which excludes K and L shell contributions.

3. Theory

3.1 *The APW calculation*

As mentioned earlier, theoretical APW Compton profiles along the three principal directions along with Lam–Platzman correction due to electron–electron correlation effects have been published by Papanicolaou *et al* [14]. In the APW formalism, within the independent particle approximation, the electron momentum distribution $\rho(\mathbf{p})$ is given by

$$\rho(\mathbf{p}) = \text{constant} \sum_{n,K,G}^{\text{occ}} \left| \int_{\text{Unit cell}} e^{-i\mathbf{p}\cdot\mathbf{r}} \psi_{n,\mathbf{k}}(\mathbf{r}) d^3\mathbf{r} \right|^2 \delta_{\mathbf{p},\mathbf{k}+\mathbf{G}}$$

where **G** is the set of reciprocal lattice vectors, **k** is a vector in the first Brillouin zone, n is the band index and $\psi_{n,\mathbf{k}}(\mathbf{r})$ is the wavefunction with band index n and wavevector **k**. To compute the valence electron Compton profile for polycrystalline sample, we have taken spherical average of the directional Compton profiles using the standard relation [14].

The spherical averaged valence electron Compton profile, after proper normalization, is added to the free atom profiles of the core electrons. The contribution of core electrons is taken directly from the tables of Biggs *et al* [19] taking into consideration the binding energies of all the shells and the recoil energy of the present experiment. The final profile is normalized to have an area of 26·67 electrons in the 0 to 7 a.u. range.

3.2 *RFA model*

The Compton profiles of 6*s* electrons of Ir were calculated within the RFA framework of Berggren [20]. The free atom Hartree–Fock wavefunctions for 6*s* electrons needed for computation were taken from tables of Fischer [21] and Herman and Skillman (HS) [22] which are numerical in nature. To preserve the charge neutrality, both the 6*s* electron wavefunctions were truncated separately at Wigner–Seitz (WS) radius 2·84 a.u. Only 33·7 and 42·8 per cent of the wavefunctions were contained within the Wigner-Seitz (WS) radius for Fischer and HS wavefunctions respectively. As in our earlier studies [10–13], the corresponding figures were higher ($\sim$90%) for 5*d* wavefunction. Therefore, the 5*d* electrons were not treated in the RFA framework. To include the crystalline effects through auxiliary function, 20 reciprocal lattice vectors were considered. The Compton profiles for 6*s* electrons with varying occupancies ($6s^x$, x ranging from 0·2 to 2·0) were computed using both the Fischer and HS wavefunctions. To obtain the total profile, contribution due to core and 5*d* electrons were suitably added and the final profiles were normalized to 26·67 electrons.

4. Results and discussion

The experimental Compton profile together with the unconvoluted theoretical results obtained using APW method with and without incorporating correlation effects are listed in table 1. The difficulties encountered in removing the systematic errors from $J(p_z)$ in the low energy side of ^{241}Am experiment, and the breakdown of impulse

Table 1. Theoretical (unconvoluted) and experimental Compton profiles of polycrystalline iridium. All quantities are in atomic units. The profiles are normalized to 26·67 electrons in the range of 0–7 a.u.. Experimental error ($\pm\sigma$) is also shown at few points. The experimental values have been derived after a complete data reduction including double scattering.

	APW		RFA $5d^{7\cdot8}\,6s^{1\cdot2}$			
p_z	Without LP	With LP	HS	Fischer	Experiment	RIF*
0·0	9·370	9·333	9·440	9·428	9·205 ± 0·040	1·521
0·1	9·358	9·320	9·392	9·374	9·198	1·455
0·2	9·282	9·244	9·283	9·268	9·153	1·270
0·3	9·194	9·157	9·038	9·028	9·061	0·998
0·4	8·999	8·962	8·783	8·779	8·919	0·685
0·5	8·715	8·679	8·323	8·330	8·727	0·378
0·6	8·476	8·444	8·019	8·021	8·490	0·119
0·7	8·192	8·163	7·857	7·870	8·211	−0·067
0·8	7·925	7·900	7·660	7·672	7·906	−0·172
0·9	7·687	7·669	7·444	7·456	7·576	−0·205
1·0	7·371	7·368	7·172	7·184	7·231 ± 0·030	−0·183
1·2	6·686	6·719	6·559	6·609	6·541	−0·130
1·4	5·971	5·600	5·980	5·987	5·915	−0·067
1·6	5·346	5·368	5·402	5·404	5·391	−0·011
1·8	4·672	4·685	4·892	4·891	4·954	0·029
2·0	4·304	4·313	4·461	4·457	4·566 ± 0·023	0·049
3·0	3·235	3·239	3·283	3·282	3·242	0·052
4·0	2·661	2·661	2·679	2·679	2·603	0·043
5·0	2·128	2·129	2·144	2·144	2·106 ± 0·017	0·028
6·0	1·645	1·645	1·663	1·663	1·657	0·001
7·0	1·267	1·270	1·284	1·284	1·261 ± 0·01	0·000

*RIF is given from 0 to 2·0 a.u. at the mesh of 0·1.

approximation for the K and L-shell electrons lead to the conclusions that symmetric profiles will not be forthcoming from this data. For this reason the high energy data was used for discussion. It is important to note that for proper comparison of experimental data with the theoretical results, the latter has to be folded with the residual instrumental function (RIF), as given in column 7, to include the residual resolution effects. Columns 4 and 5 of the table contain RFA model profiles for $5d^{7\cdot8}\,6s^{1\cdot2}$ occupancy using HS and Fischer wavefunctions respectively. It can be seen from these values that in spite of different free atom wavefunctions, these profiles are almost same. For further discussion we have taken RFA values for Fischer wavefunction into consideration. The basis of reporting RFA values for only $5d^{7\cdot8}\,6s^{1\cdot2}$ configuration is the χ^2 fitting among RFA values and the experiment. For further discussion we have called RFA for $5d^{7\cdot8}\,6s^{1\cdot2}$ configuration using Fischer's wavefunction as RFA only. The difference between APW and RFA numbers at $J(0)$ is 0·7% and becomes 1% when LP correction is incorporated indicating a difference in the solid state wavefunctions generated in APW method and modelled within the simple RFA framework. In the high momentum region (5–7 a.u.) all theoretical profiles are nearly same because this region is mainly

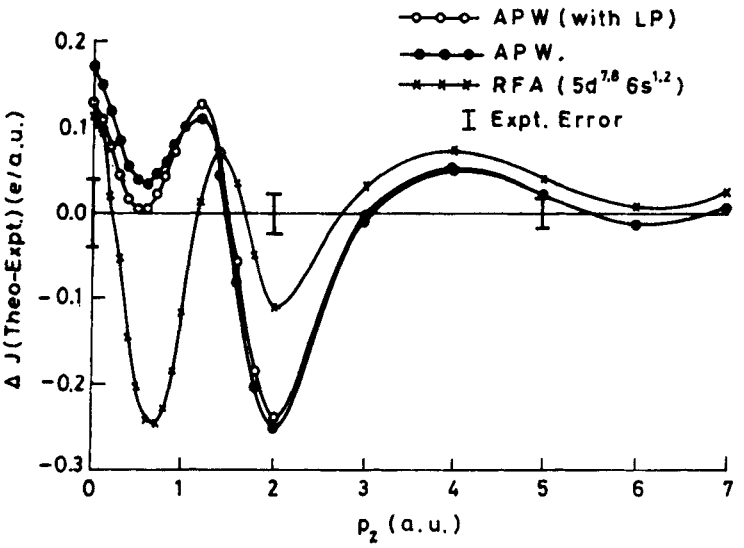

Figure 2. Difference (ΔJ) profiles for polycrystalline iridium. The theoretical result has been convoluted with the residual instrumental function (RIF).

dominated by the momentum distribution of core electrons which was same in all the calculations.

The difference profiles ΔJ calculated for experiment and convoluted theory are plotted in figure 2. This figure shows that near the Compton peak, RFA values are in better agreement with the experiment than APW method. Between 0·2–1·0 a.u., the APW calculation with LP correction shows better agreement compared to the APW without LP and RFA model. In the range 1·2 to 2·0 a.u., the RFA model is closer to experiment. In this region the incorporation of LP correction does not improve the agreement significantly. Since the LP correlation correction shifts the electrons across the Fermi momentum, consequently, the APW values with LP correction are higher for $p_z > p_F$ than those without LP correction. The differences between APW theory and experiment around 2 a.u. are larger than the RFA. The possible reason may be that Papanicolaou *et al* [14] have not included the effects of spin-orbit coupling which is important in heavy transition elements as described by Bacalis *et al* [23]. Also, Rozing *et al* [24] have observed through RAPW calculation for the two photon momentum distribution in tungsten that the inclusion of spin-orbit coupling lifts the degeneracy in bands near the Fermi surface and thus can affect the electron momentum density. It would, therefore, be important to carry out such calculation for the Ir metal also. The underestimation of the APW profile around 2·0 a.u. could also be partly due to the computational procedure used by Papanicolaou *et al*. In such calculations the essential parameter which affects the Compton profile is the number of reciprocal vectors G which determines the extent of momentum space available for all valence electrons and, consequently, the normalization factor. In the present calculation the reciprocal lattice vectors limit the 2D integration to 6·8 a.u. It could have resulted in underestimation of some high momentum components and overestimation in low momentum due

Table 2. The linewidths (FWHM) of the Compton profiles for 5*d* transition metals.

Metal	FWHM in Compton profiles			RFA configuration (best agreed)
	Experiment*	RFA	APW	
Ta [10]	3·48	3·42	3·26	$5d^{3}6s^{2}$
W [11]	3·54	3·50	3·33	$5d^{5\cdot4}6s^{0\cdot6}$
Re [12]	3·78	3·68	—	$5d^{6}6s^{1}$
Ir	4·02	3·92	3·67	$5d^{7\cdot8}6s^{1\cdot2}$
Pt [13]	4·08	3·90	3·76	$5d^{9\cdot2}6s^{0\cdot8}$

*Error = $\pm$ 0·015

to normalization of the profile. But beyond 2·0 a.u., the trend of all difference curves is almost the same.

To see the overall agreement between experiment and theoretical values based on APW model and $5d^{7\cdot8}\,6s^{1\cdot2}$ RFA calculation, we have computed χ^2 and it was found to be the least for the APW with LP correction.

On the basis of RAPW calculation, Papaconstantopoulos [25] has assigned 7.65 electrons to the 5*d* band and 0·77 electrons to the 6*s* band, the remaining 0·58 electrons have been shown to occupy 6*p* band. Davenport *et al* [26] have reported occupancies for the 5*d* transition metals using linear Slater-type orbital method with 7·51–7·19 electrons in 5*d* band, 0·67–0·92 electrons in 6*p* band and 0·82–0·89 electrons in the 6*s* band. Thus, the occupancy of 5*d* band (7·8 e) calculated by us within the RFA scheme is nearly equal to the values those predicted by Papaconstantopoulos. The difference in the 6*s* occupancy may be because of the 6*p* band also which is not considered in the RFA analysis.

Now we compare the widths of Compton profiles for 5*d* metals. In table 2 we have given full width at half maximum (fwhm) of the convoluted theoretical Compton profiles and measured Compton profiles for some 5*d* transition metals namely Ta [10], W [11], Re [12], Ir and Pt [13]. It can be noted from the table that the fwhm of the experimental Compton profiles in all these 5*d* transition metals are closer to those predicted by RFA model than the APW method. From Ta to Pt the increase in fwhm of these metals indicates that the filling in the 5*d* band gives rise to broadening of the Compton profiles. It is also supported by *d* band occupancies in the RFA model configurations (best agreed with experiment) for different 5*d* metals as given in table 2. It suggests more localization of the electron states from Ta to Pt in real space. For the neighbouring elements Ir and Pt, the fwhm of Pt experimental profile is slightly higher than Ir, while the reverse is true for RFA profiles. On the basis of photoemission studies and band structure calculation, Traum and Smith [2] have predicted that the width of the *d* bands increases (real space) when we move from Pt to Ir. The trend of experimental fwhm for Ir and Pt supports such conclusion.

5. Conclusion

Experimental Compton profile of polycrystalline iridium is presented in this paper. These results are compared with the APW calculations with and without incorporating

LP correction and RFA method using Fischer and Herman–Skillman wavefunctions. The measurement is relatively in good agreement with the APW calculation with correlation correction. RFA model favours $5d^{7.8}$ $6s^{1.2}$ occupancy. It is also seen that the choice of free atom wavefunction does not have any noticeable effect on the Compton profile. Results based on fwhm in Compton profiles indicate that the RFA model predicts occupancy in $5d$ transition metals well in agreement with our measurements. The present work clearly points towards the need for Comtpon profile calculation using fully relativistic band structure methods and measurement of directional Compton profiles which will enable more realistic comparison as all the isotropic corrections will automatically be eliminated when differences are taken.

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