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Compton profile of molybdenum

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Abstract. In this paper we report the experimental Compton profile of polycrystalline molybdenum. The measurements have been made by scattering 59·54 keV γ-rays and are compared with the recent band structure calculation of Jani *et al.* [4]. These results have also been compared with our calculation based on the renormalized-free-atom model for different $4d$–$5s$ configurations. It is found that the present experimental data are relatively in good agreement with the band structure calculation.

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

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1. Introduction

During the last two decades the electronic band structure and allied properties of molybdenum have been the subject of considerable interest and naturally numerous theoretical as well as experimental investigations have been reported on it (see, for example, [1–4]). Most recent in this context is the self-consistent calculation of Jani *et al* [4]. In this work the authors have reported the density of states, Fermi surface, charge form-factors, Compton profiles and optical conductivity for Mo metal using the linear combination of Gaussian orbitals (LCGO). They have compared their results with other calculations and with the experimental data wherever available. In particular, they could not compare their computed Compton profiles due to non-availability of experimental data and any other theoretical calculation.

In our endeavour to make a systematic study of the Compton profiles in $4d$ metals, we have previously reported our results of Zr [5], Nb [6], Rh [7], Ag [8] and Cd [9]. In this paper we present experimental Compton profile for Mo metal duly corrected for background, instrumental resolution and multiple scattering etc. In addition to this, theoretical Compton profiles computed within the renormalized-free-atom (RFA) model are also reported and both these values have been compared with the LCGO calculation of Jani *et al* [4]. Section 2 is devoted to the experimental procedure and § 3 gives the details of theoretical calculation. In § 4 we present and discuss our results.

2. Experiment

The sample used in this study was a polycrystalline sheet of 0·13 mm thickness and 99·9 per cent purity, obtained from M/s. Goodfellow Metals Ltd., U.K. The experimental set-up was the same as reported earlier by Sharma *et al* [10] and Dasgupta *et al* [11]. A brief summary of the experimental procedure is as given: 59·54 keV γ-rays from a 5 Ci annular ^{241}Am source were scattered by the sample through a mean angle of 160° ($\pm$ 2·5°) and detected by a planar intrinsic Ge detector. The momentum resolution of the spectrometer was about 0·6 a.u. Over 75,000 counts/channel were collected at the Compton peak in 42 h. The stability of the system was checked twice a day with a point source during measurement. As has been discussed in our earlier work [6], when we use 60 keV γ-rays for the study of heavier metals such as Mo then the intensity of the elastic line is quite large. The low energy tail and escape peaks due to elastic line overlap with the Compton profile and therefore, their effects have to be minimized for a proper analysis. This was achieved by the following procedure: A weak ^{241}Am source was placed in front of the Ge detector and the multichannel analyser was operated in SUBTRACT mode until the elastic line in the measured spectrum was completely removed. The background was measured by running the system without sample for 10^5 s and was then subtracted from the measurement point-by-point after scaling it to the counting time for the sample. Thereafter, the profile was corrected for the effects of instrumental resolution, sample absorption and the energy dependence of the Compton scattering cross-section following the method of Manninen *et al* [12]. The data were then converted to momentum scale to obtain the Compton profile $J(p_z)$. A Monte Carlo procedure of Halonen *et al* [13, 14] was applied to remove the contribution of both elastic as well as inelastic double scattering events. The binding energy of the K shell [15] in Mo (19·99 keV) is more than the recoil energy ($\sim$ 11 keV) and hence these ($1s$) electrons do not contribute to the Compton profile in the present experiment. They can, however, contribute via double elastic scattering for which correction has been applied as mentioned above. The experimental profile was, therefore, normalized to 17·00 electrons being the area of the corresponding free-atom profile in the momentum range of 0 to 7 a.u. excluding the contribution of $1s$ electrons [16].

3. Calculation

(a) *LCGO calculation*

Since spherically averaged Compton profile for the valence electrons in Mo were available from LCGO calculation [4], these values were directly used for this calculation. In order to obtain total Compton profile, the core contribution taken directly from the tables of Biggs *et al* [16] was added to the above valence electron profiles. The total area was equal to the value given above.

(b) *RFA*

The Compton profiles for $5s$ electrons were computed using the RFA model approach of Berggren [17]. For this calculation, Hartree–Fock wave function for $5s$ electrons was taken from the tables of Clementi and Roetti [18], truncated at the Wigner–Seitz radius 2·93 a.u. and renormalized to one to preserve the charge neutrality. It turned out that only 28 per cent of the $5s$ wave function was contained in the W–S sphere.

$J(p_z)$ due to the 5*s* electrons of Mo was computed for $5s^x$ configuration (x ranging from 0·2 to 2). For $x = 0{\cdot}2$ to 1·4 the wave function for $4d^5 5s^1$ was used and for the other cases wave function for $4d^4 5s^2$ was taken. The normalization of $J_{5s}(p_z)$ was made according to the proper number of 5*s* electrons. As usual in all 15 shortest reciprocal lattice vectors were considered. For the core and 4*d* electrons, as earlier, the Compton profiles were taken directly from the table of Biggs *et al* [16]. All the theoretical Compton profiles were normalized to an area of 17·00 electrons.

4. Results and discussion

Figure 1 shows the raw data for Mo metal accumulated in about 42 h. The elastic peak has been subtracted as per the procedure described in §2. Table 1 gives the corresponding Compton profile after applying all the corrections as mentioned in §2. Experimental errors are also given for some values. In columns 5 and 6 the experimental profile before and after applying the double scattering (DS) correction on a sample of 0·13 mm thickness is given. It is observed that the effect of DS correction is not negligible. It sharpens the Compton profile and $J(0)$ is increased by about 1·5%. Also given in this table are the theoretical values for LCGO (column 4) and RFA (columns 2 and 3). Due to lack of space the results from RFA model for only two different

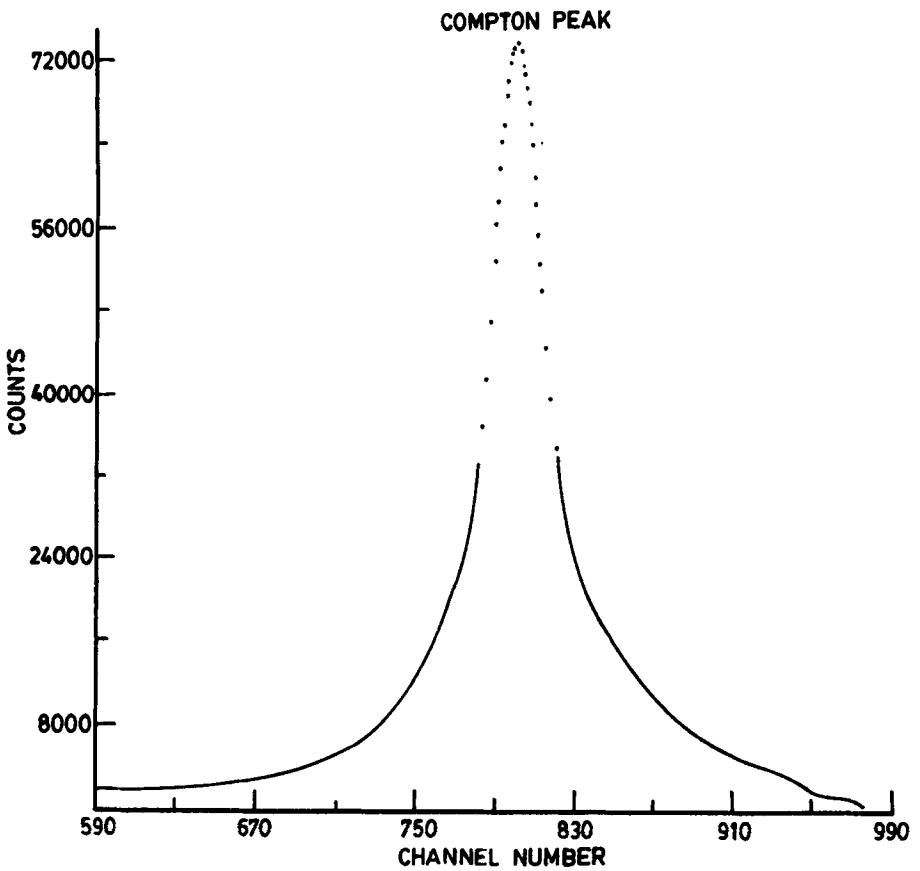

Figure 1. Raw experimental data for polycrystalline molybdenum. The elastic peak has been subtracted.

Table 1. Unconvoluted theoretical and experimental Compton profiles $J(p_z)$ of polycrystalline molybdenum. All quantities are in atomic units. All values are normalized to 17·00 electrons which corresponds to the area under free atom Compton profile (except $1s^2$) for the momentum range between 0 to 7·0 a.u. D.S. means correction for double scattering.

				Experiment (0·13 mm thickness)		
P_z	Core + RFA $4d^{5\cdot4}5s^{0\cdot6}$	Core + RFA $4d^{5\cdot2}5s^{0\cdot8}$	LCGO	Before DS	After DS	RIF
0·0	7·351	7·404	7·472	7·205	7·315 ± 0·046	0·2009
0·1	7·318	7·377	7·446	7·191	7·302	0·1861
0·2	7·245	7·297	7·332	7·144	7·254	0·1468
0·3	7·082	7·156	7·161	7·022	7·125	0·0931
0·4	6·893	6·947	6·963	6·846	6·940	0·0391
0·5	6·569	6·653	6·724	6·662	6·749	−0·0035
0·6	6·326	6·294	6·495	6·448	6·529	−0·0278
0·7	6·089	6·043	6·255	6·162	6·237	−0·0327
0·8	5·817	5·775	5·999	5·849	5·915	−0·0261
1·0	5·208	5·175	5·347	5·216	5·259 ± 0·039	0·0038
1·2	4·558	4·532	4·494	4·516	4·530	0·0119
1·4	3·955	3·934	3·862	3·894	3·898	0·0029
1·6	3·434	3·418	3·273	3·353	3·345	−0·0045
1·8	2·987	2·983	2·828	2·922	2·905	−0·0029
2·0	2·647	2·645	2·566	2·617	2·595 ± 0·028	0·0011
3·0	1·816	1·816	1·802	1·790	1·769	
4·0	1·427	1·427	1·427	1·432	1·414	
5·0	1·099	1·099	1·098	1·129	1·114 ± 0·017	
6·0	0·829	0·829	0·829	0·876	0·862 ± 0·013	
7·0	0·629	0·629	0·629	0·665	0·647 ± 0·012	

electron configurations namely $4d^{5\cdot4}5s^{0\cdot6}$ and $4d^{5\cdot2}5s^{0\cdot8}$ are given and these are close to our measurement values. To compare these theoretical values (columns 2–4) with that of experiment (column 6) they have to be first convoluted with the 'residual instrumental function' (RIF), because a complete deconvolution cannot be performed due to the statistical noise in the experiment [19]. Accordingly, we have convoluted all these theoretical results (columns 2–4) with the RIF of our instrument given in column 7 (for possible use by other workers). The difference (ΔJ) between theoretical values (convoluted with RIF) and our experiment in low momentum region are plotted in figure 2. It can be seen in this figure that at $p_z = 0$ and 0·1 a.u. the RFA calculation with $4d^{5\cdot4}5s^{0\cdot6}$ configuration shows very good agreement while between 0·2 and 1·0 a.u. the LCGO calculation gives the best agreement. In the region 1·2–2·0 a.u., the RFA values are systematically higher than experiment while for LCGO calculation the trend is reversed. Between 2·0 and 4·0 a.u. the LCGO model again gives very good agreement. Regarding values in the high momentum region, as given in table 1, it has been found that these theoretical values after convolution with RIF remained almost unchanged. Thus, the values given in this table can safely be used for comparison in this high region. It is seen that all theoretical values are nearly the same which is easily understood because the contribution from inner electrons, excepting 4*d* electrons, is the same in all calculations and the contribution of '4*d*' electrons is not substantial in this region.

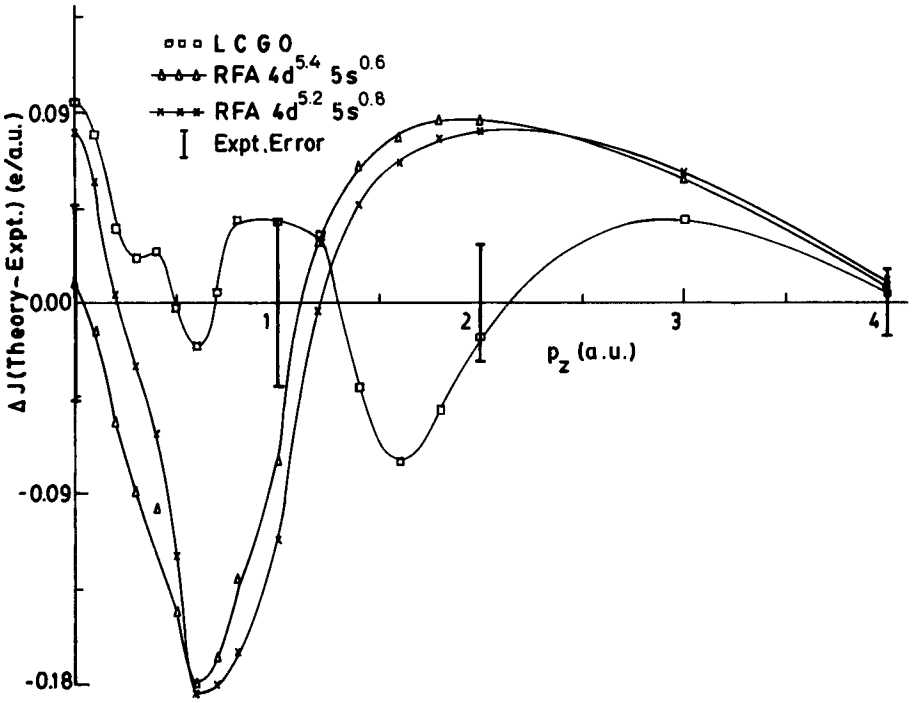

Figure 2. Difference (ΔJ) profiles for bcc molybdenum. The theoretical result has been convoluted with the residual instrumental function (see text).

From the values given in table 1, it is obvious that, although there is a good agreement between theory and experiment for p_z equal to 4 and 5 a.u. there are deviations in the region 5–7 a.u. It may be worthwhile to point out that we had observed similar deviations in our previous studies on other 4*d* metals [5, 7] and references therein) but we shall return later to examine the possible origin for this systematic effect.

To obtain an estimate of overall agreement between theory and experiment for all cases, we have calculated χ^2 (which is equal to

$$\sum_{p_z=0}^{7\cdot0} \left| \frac{\Delta J(p_z)}{\sigma(p_z)} \right|^2$$

with $\sigma(p_z)$ representing the corresponding experimental error). It turned out that among RFA calculations the value of χ^2 was lowest for $4d^{5\cdot2}5s^{0\cdot8}$. However, for LCGO calculation χ^2 was much smaller which clearly suggests that the present data is in much better agreement with the LCGO calculation compared to RFA model. There however, remain differences between this theory and the present experiment which at some points are larger than the experimental errors even during 0 to 4·0 a.u. Regarding the differences observed at $p_z = 0$ and near it, the theoretical values are larger than the experiment. This feature is in agreement with the observation of Cardwell *et al* [20] and Cardwell and Cooper [21] on some simple and transition metals of the 3*d* group when the experimental data were compared with the band theoretical calculations performed within the frame work of independent particle approximation (IPA). It has now been established that for a proper description and to explain the above discrepancy, it is necessary to include $e^- - e^-$ correlations which

affect the electron momentum density (emd) by raising some electrons from levels just below ($p < p_F$) the FS to levels just above ($p > p_F$) it without shifting the discontinuity at $p = p_F$ (see, also Sunderarajan *et al* [22]. Detailed calculations made on transition metals having partially filled *d*-states (V, Cr, etc.) have shown that this correlation correction (like emd) is also anisotropic in such cases. For Cr, $e^- - e^-$ correlation contribution was 1 to 3 per cent of the total $J(p_z)$ at $p_z = 0$ and changed sign from initially negative ($p < p_F$) to positive value for $p > p_F$. (see, for example, Cardwell *et al* [20], Wakoh and Matsumoto [23]. For Mo, no such calculation is reported yet to our knowledge. However, on the basis of the numerical values published for Cr, it seems that $e^- - e^-$ correlation would decrease the theoretical values at least by about 0·07 e/au (~ 1 per cent) at $p_z = 0$ improving thereby the agreement in the region between 0 and 1 a.u. In view of the opposite sign of the correction for $p_z > 1{\cdot}0$ a.u., the theoretical values for p_z up to 2·0 a.u. would then also come closer to the experiment. Also, for $p_z > 4$ a.u., this positive contribution might improve the agreement, because the theoretical values are slightly smaller than experiment in this region. It may further be mentioned that the spherically averaged values given by Jani *et al* [4] have been obtained using the approximate formula which may not be very reliable in the case, such as the present one, where electron momentum density is highly anisotropic. In view of all these, the differences observed are not unreasonable but the picture will become more clear only when measurements on single crystals and a detailed theoretical analysis of $e^- - e^-$ effects are also carried out for Mo.

Now we focus on the disagreement between theory and experiment in the high momentum region. Some of the possible causes for this are (i) non-validity of impulse approximation (IA), (ii) residual multiple scattering, (iii) continuous spectrum of bremsstrahlung emitted by the photoelectrons and (iv) low energy tail in the primary radiation due to self-scattering within the source.

Regarding the non-validity of IA, for 60 keV gamma rays (as in present experiment) the 1*s* electrons of Mo do not contribute to Compton scattering within -7 to $+7$ a.u. Moreover, for Zr, as pointed out by Manninen *et al* [24], these effects were insignificant for 1*s* electrons. A prescription to estimate quantitatively the effect of such a correction to the Compton profiles for 1*s*, 2*s* and 2*p* electrons has been developed by Holm and Ribberfors [25]. It has been theoretically deduced that the first correction to the impulse approximation can be expressed in terms of a function ε/q where $\varepsilon = n(2m|E_{n1}|)^{1/2}$, E_{n1} being the binding energy of the $n1$ subshell, and q is the momentum transfer. In the present case the value of momentum transfer at $p_z = 0$ is about 28·5 a.u. and *L*-shell binding energies for Mo are about 2·7 keV. Thus, the value of ε/q is about 0·3 and hence following the conclusion of Holm and Ribberfors [25] the maximal error is $20\varepsilon/q$ for *L* shell electrons, given in per cent of $J(0)$ within IA. Using the *L* shell contribution at $J(0)$ from the tables of Biggs *et al* [16] and including the opposite sign of 2*s* and 2*p* contributions, the calculated error in the IA comes out to be about 0·005 e/a.u. at $J(0)$ which is smaller than the statistical error of our experiment. We can, therefore, ignore these effects and safely conclude that IA can be considered to be valid for the *L*-electrons of Mo. It is worthwhile to point out that in a recent work, Manninen and Paakkari [26] have arrived at a similar conclusion for Ag and it is only reasonable to expect the same for Mo also.

As for the multiple scattering contribution, Monte Carlo prescription of Halonen *et al* [13, 14] as pointed out earlier, takes care of double elastic as well as inelastic events. Although, we have not made any correction for higher order scattering, but as discussed by Halonen *et al* [13, 14], the fractional contribution from higher than

second order scattering is about 1/4 times of the ratio of double to single scattering. In the present case the ratio of double to single scattering turned out to be 3·6 per cent suggesting that the fractional contribution from higher than the second order scattering should be less than one per cent. This is also supported by a recent work of Das *et al* [27] wherein it was concluded that the relative intensity for triple scattering would saturate at $\sim 1\%$ for $Z > 18$ as is the case in the present work. Thus, the contribution due to higher than double scattering will naturally be very small and of the order of experimental errors. In order to look for the contribution due to residual multiple scattering, the statistical accuracy would have to be improved by at least a factor of 3 or more. At the present level of precision, we cannot establish this contribution in this work unambiguously excepting that the total contribution is less than 1 per cent. But this can be one of the possible causes of the discrepancy between theory and experiment as discussed earlier.

In order to estimate the effect due to bremsstrahlung produced inside the sample due to photoelectrons (as this is the leading process compared to Compton process), we have calculated the ratio of the intensities due to BR (I_{BR}) and Compton scattering (I_C) following the method of Alexandropoulos *et al* [28]. It was found that this ratio I_{BR}/I_C was around 3 per cent. However, most of the contribution to this came from K-shell and their bremsstrahlung contribution vanishes above 40 keV whereas the energy of the Compton scattered photons due to valence electrons lies in the range beyond this value. There would, however, be bremsstrahlung contribution from electrons in the L, M, N etc. shells. This contribution in the region of Compton profile was estimated to be around 0·2 per cent. Thus, we can ignore the contribution of this effect in the present case.

The presence of low energy contamination in the monochromatic gamma-ray sources due to self scattering has been established unambiguously in recent years [29]. Direct measurements of energy spectrum of ^{198}Au source have confirmed the presence of a low energy tail and its effect on Compton profile has been studied in detail to allow corrections for this [30]. However, for the ^{241}Am source which was used in the present work (5 Ci annular geometry), the same is not true. The source consists of AmO_2 in a ceramic matrix with stainless steel enclosure and the exact composition of this source is not available. Thus, reliable simulation is not possible. However, measurements by Manninen *et al* [29] on a 2 mm thick ^{241}Am source have confirmed the presence of low energy radiation but the tail integral is only 4 per cent. The effect of this is to produce an asymmetry between high and low energy sides but as pointed out by Rollason *et al* [30] it is accepted that the data from the high energy side of the Compton profile are relatively little affected by this contamination. The data presented here also refer to the high energy side as mentioned above and thus we can expect that the effects due to self-scattering will be minimal. But this does not rule out in any way the possibility that the observed discrepancy in the high momentum region could, at least partly, be due to this. We are examining this aspect in more detail and the conclusion would be reported later.

It is interesting to note that Hosson [31] suggested the electron distribution in Mo metal to be close to $4d^5 5s^1$ in his calculation using scattering theory while Papaconstantopoulos [32] has reported 0·61 and 0·32 electrons in 5*s* and 5*p* bands suggesting nearly 5 electrons in 4*d* band. These values are no doubt close to our results from the RFA calculation ($4d^{5\cdot2} 5s^{0\cdot8}$) however, there are obvious differences between RFA calculation and experiment. Also the LCGO values are a bit higher than experiment for $p_z = 0$ and 0·1 a.u. and we cannot assign any reason to it.

5. Conclusion

In this work we have reported experimental data on Compton profile of Mo metal. The experimental data are in relatively good agreement with the LCGO calculations. Measurements particularly on single crystals would be useful to understand the electronic structure in Mo because in that case the experimental problems discussed earlier namely, the multiple scattering, the scattering within the source, bremsstrahlung contribution etc. would be eliminated particularly when directional differences are considered. Further, a detailed theoretical analysis of $e^- - e^-$ correlation along the lines of Wakoh and Matsumoto would be essential so that the band theoretical values for the directional Compton profiles could be suitably compared with the experiment. It is hoped that our work would simulate further interest in this direction.

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