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Electron-momentum distribution in zirconium

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The electron-momentum distribution in hexagonal-close-packed zirconium has been studied for the first time with use of a Compton-scattering technique. Measurements have been made by scattering 59.54-keV γ rays. Theoretical computations have been carried out with use of the renormalized-free-atom model for various 4*d*-5*s* configurations. Best agreement between theory and experiment is found if the electron configuration is chosen as $4d^35s^1$.

I. INTRODUCTION

Zirconium is one of the transition metals in the second series and crystallizes in the hexagonal-close-packed structure ($a=6.106$ a.u., $c=9.728$ a.u.).[1] Like other hexagonal-close-packed (hcp) transition metals (Ti, Y, and Hf, etc.), the electron band structure and Fermi surface of this metal are complicated and less well understood in comparison to their cubic counterparts. Despite difficulties due to unaxial symmetry and two atoms in the unit cell, detailed calculations have been reported for Zr,[2–6] and their predictions compared with the available experimental data on *K*-edge photoabsorption;[7] Fermi surface,[8] optical conductivity, and superconductivity.[6]

Electron momentum density (EMD) is also an important ground-state property because of its direct relationship with the electronic wave function, and Compton scattering is one of the most direct ways to investigate it.[9] Several measurements on Compton profile and the electron momentum densities of cubic as well as hcp 3*d* transition metals have been reported within the last decade.[10–12] To interpret these, calculations based on different methods such as band structure, LCAO, free-electron theory, and the renormalized-free-atom (RFA) model, etc., have been performed and useful information has been obtained regarding their electron structure.

In recent years the Compton scattering technique has been applied to 4*d* metals also.[13–18] These, however, do not cover any of the hcp metals. It was therefore thought of interest to investigate the case of hcp zirconium. Since the RFA model is known to be a reasonable compromise between elaborate band structure and simple atomic methods, we have also attempted to interpret our experimental results in terms of the RFA model. Accordingly, Compton profiles have been calculated for several 4*d*-5*s* electron configurations in Zr. In Sec. II we describe briefly the method of measurement and in Sec. III, the RFA calculation. In Sec. IV we present our results and discussion.

II. EXPERIMENT

The experimental setup used in this work is the same as reported earlier by Sharma *et al.*[18] and Das Gupta *et al.*[19] The salient features are as given here: γ rays from a 5-Ci annular ^{241}Am source are scattered at an angle of 159° (±2.5°) by a 0.01-cm-thick sheet of polycrystalline zirconium metal. The scattered radiation is detected using an intrinsic planar Ge detector. The momentum resolution of the spectrometer was about 0.6 a.u. [full width at half maximum (FHWM)]. Over 60 000 counts/channel were accumulated at the Compton peak in a period of 2 days. The stability of the system was checked twice a day with a point source during the measurement.

In comparison to the Compton measurements on light elements the use of 60-keV gamma rays for heavier elements such as Zr results in a large intensity of the elastic line (Fig. 1). The low-energy tail and escape peaks of the elastic line overlap with the Compton profile. The contribution of this line was avoided in the following way:[16] A weak ^{241}Am source was placed in front of the Ge detector and the multichannel analyzer 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 a sample for 10^5 sec and was subtracted from the measurement point by point after scaling it to the actual counting time. Thereafter, the profile was corrected for the effects of instrumental resolution, sample absorption, and energy dependence of the Compton scattering cross section following the method of Paatero *et al.*[20] The data was then converted to momentum scale to obtain the Compton profile $J(p_z)$. A Monte Carlo procedure of Halonen *et al.*[21] was used to remove the contribution of elastic and inelastic double scattering events. Since the binding energy of the *K* shell[22] in Zr (17.997 keV) is more than the recoil energy (~ 11 keV), the 1*s* electrons do not contribute to the Compton profile in the present experiment. The experimental profile was therefore normalized to 16.33 electrons, being the area of the corresponding free-atom profile in the momentum range of 0 to 7 a.u., excluding the contribution of 1*s* electrons.[23]

III. CALCULATION

The computation of Compton profiles for hcp metals in the RFA model is well known[10,24] and needs no repitition. We shall describe the procedure only briefly here. The Hartree-Fock wave function for 5*s* electrons was taken from the tables of Clementi and Roetti,[25] truncated at the Wigner-Seitz (WS) radius (3.35 a.u.). and renormalized to unity to preserve charge neutrality. It turned out that only 32% of the $5s^1$ wave function was contained in the WS sphere while for the $4d$ wave function this number is about 85%. In the case of the $4d^2 5s^2$ wave function, corresponding numbers were 35% and 90%, respectively. Accordingly, only $5s$ electron wave-functions were considered in the RFA scheme.

Following Berggren *et al.*,[10] Compton profiles due to $5s$ electrons were computed for $5s^1$, $5s^2$, and several other cases using the formula

$$J_{5s}(p_z)=4\pi \sum_{n=0}^{\infty} |\psi_0^c(\mathbf{K}_n)|^2 G_n(p_z) , \qquad (1)$$

where $\psi_0^c(\mathbf{K}_n)$ is the Fourier transform of the RFA wave function and $G_n(p_z)$ is the auxiliary function involving reciprocal-lattice vectors $\mathbf{K}_n$, Fermi momentum p_F, the number of points in the nth shell in reciprocal space, and the position of the atom in the unit cell. (For further details we refer the reader to Refs. 10 and 24.) For the cases when the number of $5s$ electrons were taken between 0.2 and 1.4, the wave function for the $4d^3 5s^1$ configuration was used, and for others the wave function for the $4d^2 5s^2$ configuration was taken. The normalization of the $J_{5s}(p_z)$ was made according to the proper number of $5s$ electrons. As was done for Pd (Ref. 18), in all, 15 shortest reciprocal-lattice vectors were considered in the sum in Eq. (1). For the core electrons and also $4d$ electrons, the Compton profiles were taken directly from the table of Biggs *et al.*[23] The theoretical profiles so obtained were all normalized to an area of 16.33 electrons.

IV. RESULTS AND DISCUSSION

Figure 1 shows the raw data accumulated in about 43 h. The broad peaks around channel no. 804 having a FWHM of ~32 channels is due to Compton scattered events and the sharp peak on the extreme right is due to elastic scattering. The data after applying all the corrections as per Sec. II is presented in Table I. Errors for some points are also given. Also presented in this table are theoretical results for five different electron configurations, namely, $4d^{3.4}5s^{0.6}$, $4d^{3.2}5s^{0.8}$, $4d^3 5s^1$, $4d^{2.8}5s^{1.2}$, and $4d^2 5s^2$. Comparing first the experimental data given in columns 8 and 9 it can be seen that the effect of double scattering is not negligible despite the fact that the absorption coefficient of Zr for 60-keV γ rays is large and the thickness of the sample was 0.01 cm. The correction due to double scattering (DS) increases the $J(0)$ value by 0.045 e/a.u. It may be pointed out that in the case of silver, Sharma *et al.*[17] found this correction to be 0.065, which can be understood because of a different thickness (0.125 mm) and a larger value of absorption coefficient (μ) in Ag.

Next we consider the comparison of the theoretical values with experiment. Here it is worthwhile to mention that in order to compare Compton profile calculations with the "deconvoluted" experiment it is necessary to convolute the theory with the "residual instrumental function" (RIF), because a complete deconvolution cannot be performed due to the statistical noise in the experiment.[20] Accordingly, we have convoluted all the theoretical results (columns 2–6) with the RIF of our instrument (column 7), as given in the Table I for possible use by other workers. The RIF-convoluted theoretical values have also been normalized to 16.33 electrons and then compared with the experimental data of column 9 (DS corrected). The difference profiles (ΔJ) exhibiting the difference between theory (convoluted as above) and experiment for various configurations are plotted in Fig. 2. It can be seen that, between 0 and 0.2 a.u., $4d^{3.2}5s^{0.8}$

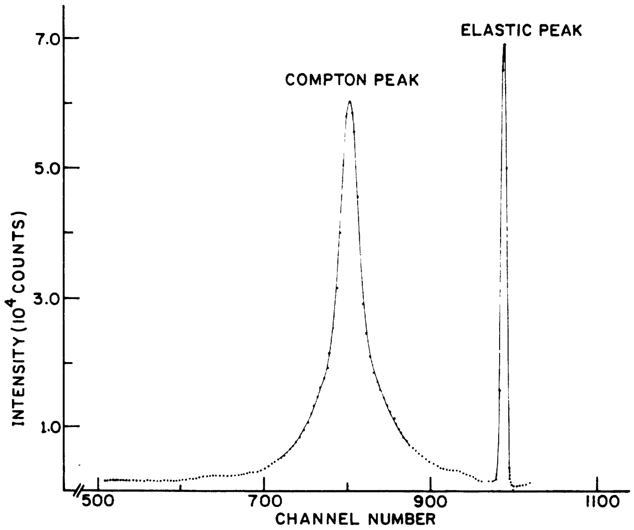

FIG. 1. Energy distribution of 59.54-keV photons from a ^{241}Am source scattered at 159° (±2.5°) from polycrystalline Zr. Each channel corresponds to about 63 eV.

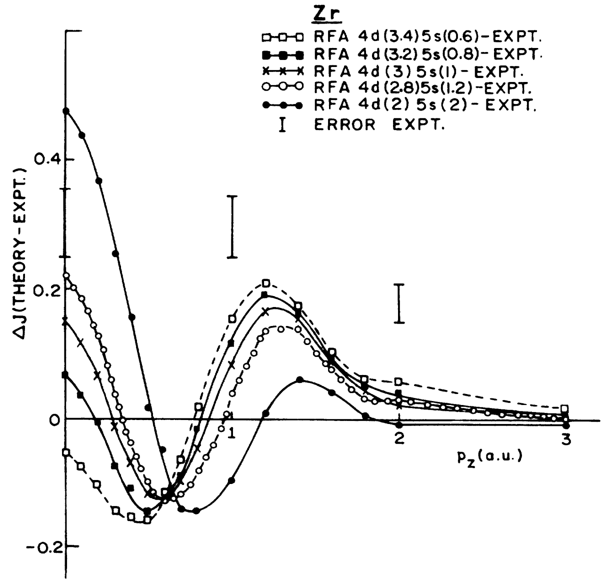

FIG. 2. Difference (ΔJ) profiles for hcp zirconium. The theoretical result has been convoluted with the residual instrumental function (see text).

TABLE I. Theoretical and experimental Compton profiles of polycrystalline zirconium. All quantities are in atomic units. The values have been normalized to 16.33 electrons, being the area under $J_{\text{total}}-J_{1s^2}$ between 0 and 7 a.u. DS means double scattering. The residual instrumental function (RIF) is also given (see Ref. 20).

p_z	Core + RFA $4d^{3.4}5s^{0.6}$	Core + RFA $4d^{3.2}5s^{0.8}$	Core + RFA $4d^{3}5s^{1}$	Core + RFA $4d^{2.8}5s^{1.2}$	Core + RFA $4d^{2}5s^{2}$	RIF of expt.	Experiment Before DS	Experiment After DS
0.0	7.411	7.503	7.568	7.632	7.854	0.2009	7.360	7.405±0.053
0.1	7.358	7.451	7.516	7.580	7.801	0.1561	7.333	7.377
0.2	7.245	7.337	7.404	7.467	7.688	0.0931	7.232	7.279
0.3	6.995	7.086	7.155	7.218	7.438	0.0391	7.058	7.108
0.4	6.710	6.801	6.873	6.938	7.160	−0.0035	6.820	6.870
0.5	6.329	6.313	6.391	6.459	6.686	−0.0278	6.525	6.574
0.6	6.113	6.062	6.012	5.993	6.231	−0.0327	6.186	6.232
0.7	5.843	5.797	5.752	5.705	5.526	−0.0261	5.818	5.859
0.8	5.544	5.504	5.463	5.422	5.251	−0.0026	5.435	5.471
1.0	4.874	4.844	4.813	4.781	4.652	0.0107	4.679	4.702±0.047
1.2	4.211	4.189	4.167	4.144	4.052	0.0086	4.001	4.016
1.4	3.619	3.603	3.588	3.572	3.509	−0.0019	3.449	3.457
1.6	3.137	3.125	3.113	3.102	3.059	−0.0046	3.026	3.029
1.8	2.765	2.755	2.746	2.736	2.704	−0.0006	2.707	2.704
2.0	2.493	2.486	2.479	2.471	2.444	0.0019	2.466	2.461±0.031
3.0	1.815	1.814	1.812	1.812	1.806		1.814	1.803
4.0	1.404	1.404	1.403	1.403	1.401		1.442	1.433
5.0	1.045	1.044	1.044	1.044	1.042		1.091	1.081±0.019
6.0	0.770	0.770	0.770	0.769	0.768		0.813	0.803
7.0	0.576	0.576	0.576	0.575	0.574		0.616	0.607

shows the best agreement between theory and experiment, while the differences are largest for $4d^2 5s^2$. The corresponding values of ΔJ for $4d^{3.4}5s^{0.6}$ are all negative up to 0.8 a.u. and then become positive and remain larger than for all other cases. In the 0.2–1.0 a.u. region the $4d^3 5s^1$ configuration is closer to experiment, while between 1.0 and 2.0 a.u., the best agreement is seen for the $4d^2 5s^2$ configuration. Between 2 and 3 a.u. momentum the overall trend of the "difference profile" is identical in all cases and the difference ΔJ decreases as the "$4d$" contribution decreases. Also for each case the difference between theory and experiment decreases as we move towards the higher-momentum region, being lowest for the $4d^2 5s^2$ configuration.

To determine the most favored configuration, we have calculated a quantity Δ^2 given as $\sum_{p_z=0}^{7} |\Delta J(p_z)|^2$, a measure of the overall deviation. It turned out that Δ^2 was smallest for the $4d^3 5s^1$ configuration, and the corresponding values for $4d^{3.2}5s^{0.8}$ and $4d^{2.8}5s^{1.2}$ were a bit higher. Therefore, it can be concluded from this study that the most favored configuration for hcp zirconium can be taken as $4d^3 5s^1$. This is quite different from $3d$ hcp metals namely Sc, Ti, and Co, in which $4s^2$ configuration was favored over $4s^1$, without exception.[10,12]

It may be mentioned that Jepsen *et al.*[4] in their calculation of the electronic structure of Zr using the linear-muffin-tin orbital method obtained a value of nearly 2.8 for the number of d electrons (n_d). Interestingly, this agrees well with the present values. The results of Jepsen *et al.*,[4] however, cannot be compared directly with our work because these authors did not compute the Compton profile for Zr. A small difference of 0.2 electron in d-band occupancy is not unexpected in view of the fact that Jepsen *et al.* have considered the occupancies of s, p, and d bands also, whereas we have not included "$5p$" occupation. As regards the previous EMD calculation, Iyakutti *et al.*,[5] have calculated the momentum density distribution of positron annihilation along the C axis. These results are influenced strongly by the wave function for the positron and therefore cannot be directly compared with this work. It would have been most useful if similar calculations for the Compton profile were available.

In the high momentum region (4–7 a.u.), it is seen in Table I that all theoretical profiles are identical. It has to be so because the contribution in this region comes mostly from the inner core electrons, which is the same in all configurations. It also turns out that changes in their values given in Table I after convoluting these with RIF are negligible. We can therefore safely consider the values given in Table I for comparison with experiment in this region. It is seen that the theoretical values are very close to the experiment from 4 to 7.0 a.u. A small difference of 0.02 to 0.03 e/a.u. can be seen but the overall agreement is remarkable. This is not unexpected because the inner electrons are reasonably described in the metal also by the free-atom wave functions. The values taken from the tables of Biggs *et al.*[23] are based on an electron wave function in which relativistic effects are included. Also, as mentioned earlier, the $1s$ electrons do not contribute in this experiment. They can, however, contribute through double scattering via elastic process. This contribution has been already considered in the double scattering correction. The close agreement between theory and experiment in this region in a way is suggestive of the fact that the impulse approximation can be considered valid for L electrons, and the Compton profile for $4d$ electrons in metals is close to the free-atom value.

The data presented in Table I corresponds to p_z values on the low-energy transfer side. Considering the fact that the binding energies of L shells[22] are 2.532, 2.307, and 2.222 keV and the recoil energy (RE) varies from 11 to 7 keV for $p_z = 0$ to $(+)7$ a.u., the ratio of recoil to binding energy is always more than 2 and increases to 4 as we go towards the low-momentum region. Thus, there seems no reason to doubt the validity of impulse approximation and the present analysis of $4d$-$5s$ occupancies can be considered reliable to the extent that $4d$ electrons have been considered in the simple atomic model. The simple RFA model has thus been able to provide a reasonable description of the Compton profile for Zr metal. In the case of $3d$ metals it has been already observed that the best RFA results are close to the sophisticated band-structure calculations and experiment. This seems to be true for $4d$ metals also. In a recent work it was noted that for Pd the $5s$ occupancy as deduced from the RFA model turned out to be in good agreement with the conclusion of de Haas and van Alphen and other studies.[18] It would be therefore interesting to carry out a detailed computation of the Compton profile for Zr using linear muffin-tin orbitals or another accurate method. Also, measurements particularly on single crystals can help in understanding the electron structure in Zr.

V. CONCLUSION

In this paper we report for the first time the experimental and theoretical electron momentum distribution for hcp zirconium. It is found that the Compton scattering data favors $4d^3 5s^1$ configuration. This work also suggests that like $3d$ metals the simple RFA model works reasonably well for the case of hcp $4d$ transition metals. However, more refined calculations and measurements are needed to provide a complete interpretation of electron structure in such metals.

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