Electron Momentum Density in Europium Using a ^{137}Cs Compton Spectrometer

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The isotropic Compton profile of europium, the most reactive lanthanide, has been measured at a resolution of 0.40 a.u. using 661.65 keV gamma-rays. In the absence of a band structure-based Compton profile, the experimental data are compared with renormalised-free-atom (RFA) and free electron models. It is seen that the RFA model with e^--e^- correlation agrees better with the experiment than the free electron models. The first derivatives of the Compton profiles show the hybridization effects of s-, p-, d-, f-electrons. From our RFA data we have also computed the cohesive energy of europium.
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Key words: Compton Profile; Electron Momentum Density; Lanthanides; Cohesive Energy.

1. Introduction

The unusual magnetic properties of rare-earth metals, exploited in modern applications, are a consequence of their peculiar electronic structure. Their outer shells, including 5s, 5p and 6s, are completely filled, whereas the 'inner' 4f shell is open. The outer electrons primarily determine the chemical behaviour, and hence most of the rare-earth metals show similar chemical properties. Europium (Eu), which is one of the rarest of the rare-earth metals, is one of the most reactive metals of the rare earth series. It ignites in air at about 150 °C [1]. The electronic behaviour of Eu is a suitable subject of investigation because of its special electronic configuration [Xe]4f^{7}6s^2 with half-filled 4f orbital. It is well established that there are two types of f-electrons in the lanthanides: core-like f-electrons and delocalized band-like f-electrons which participate in bonding. Earlier theoretical and experimental work on lanthanides is mainly dealing with their valence band and photoelectron spectra, Rydberg states, density of states, resonant excitations, cohesive properties, band structure calculations employing KKR and self-interaction-corrected local spin density (LDA) approximation [2 – 9].

In a Compton scattering experiment [10], within the impulse approximation the double differential Compton scattering cross-section for detecting the energy transfer and solid angle of the outgoing photon is given by

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\hbar\omega_2\mathrm{d}\Omega_2}\right) = \sum_{nl} C(\hbar\omega_1, \hbar\omega_2, \phi)\, J_{nl}(p_z), \quad (1)$$

where C is a conversion factor depending on experimental parameters like the scattering angle, incident and scattered energies, and $J_{nl}(p_z)$ the Compton profile, specified with quantum numbers n and l, which is

$$J_{nl}(p_z) = \int_{p_x}\int_{p_y} \rho_{nl}(\vec{p}_1)\mathrm{d}p_x\mathrm{d}p_y, \quad (2)$$

where $\rho_{nl}(\vec{p}_1)$ is the initial momentum density of the target electrons and is related to the real space wave functions, and p_z is the component of the electron momentum along the scattering vector (chosen as z-axis).

Quite recently our group has reported ^{137}Cs based Compton profile data on four lanthanides, namely Sm [11], Tb [12], Ho [13], and Yb [14]. In our endeavour to extend the study of the Compton profiles and hence that of the electronic properties of lanthanides, in this paper we present the first Compton profile measurement on Eu using 661.65 keV gamma-rays from a ^{137}Cs source. The limitations of the conventional ^{241}Am based spectrometer in Compton profile measurements of the lanthanides have been discussed in [10, 14]. Besides investigating the electron

momentum density in Eu, in this paper we also report the cohesive energy of this lanthanide. Due to the high chemical reactivity, ignition in air at low temperature and the requirement of ultra high vacuum conditions in growing the required size (about 13 mm diameter and 3 mm thickness) of single crystals of Eu, we have performed the present measurement on a polycrystalline sample.

Henceforth all quantities are given in atomic units (a. u.), where $m = \hbar = 1$, $c = 137.036$ and 1 a.u. of momentum is $1.99289 \cdot 10^{-24}$ kg m s^{-1}.

2. Experimental

A gamma-ray Compton spectrometer (see [15] for more details) with a 20 Ci ^{137}Cs source was used. Collimated gamma-rays of 661.65 keV were allowed to fall normally on the sample, and the Compton-scattered gamma-rays were detected by a HPGe detector (Canberra, GLP0210) at a large scattering angle ($160^\circ \pm 0.6^\circ$). The sample, which was a polycrystalline sheet of 99.9+% purity, 0.4 mm thickness and 12×12 mm^2 cross-section, was fixed between the air-tight folds of a thin mylar foil under argon. The raw Compton data were then recorded by a multichannel analyzer (Canberra, Accuspec B) with a channel width of 0.035 a.u. on the electron momentum scale. The overall momentum resolution of the spectrometer was 0.40 a.u. [Gaussian full width at half marinum (FWHM)], which is much better than that of the conventional ^{241}Am based Compton spectrometers (0.60 a. u.).

The sample was exposed for about 133 h to yield an integrated Compton intensity of 7.45 million photons in the range -10 to $+10$ a. u. The electronic drift in the detection system was checked from time to time and was negligible. It is worth mentioning here that, due to the extremely high chemical reactivity of Eu with air, we have limited our measurement to a relatively short duration. Nevertheless, the present statistics are more than sufficient in the momentum range up to 4 a. u., which is sensitive to the behaviour of the valence electrons.

To extract the true Compton profile from the raw data, a computer code developed by the group of Prof. Cooper in U.K. [16] was used to perform the data reduction. The present raw data were corrected for background, detector efficiency, sample absorption, Compton cross-section, instrumental resolution, multiple scattering, etc. For the background corrections, the data were recorded separately for about 76 h after removing the sample. We maintained the experimental conditions. Thereafter, the measurement time of the background was scaled to the exposure time of the sample to perform the background correction. The instrumental resolution correction was restricted to stripping off the low energy tail from the measured data, leaving the theoretical profile to be convoluted with a Gaussian FWHM of 0.40 a. u. (experimental resolution). Corrections for double and triple scattering in the sample were performed using the Monte Carlo simulation code of the same group [17]. The effect of multiple scattering was found to be 2.8% in the momentum region -10 to $+10$ a.u. Further, in addition to the usual data analysis in Compton spectroscopy [16, 17], we have also corrected the experimental profile for the contribution due to bremsstrahlung (BS) from the photo and Compton recoiled electrons liberated in the sample by the 661.65 keV incident gamma-rays. The methodology for the BS correction in high energy Compton scattering experiments (like the present one) has been developed by our group [15, 18]. Using these prescriptions, 0.26 electrons (area under the BS background profile) were found to contribute to BS in the momentum range -7 to $+7$ a.u. Thereafter, the profile was normalized to 19.50 electrons, which is the free atom profile area [19] from 0 to 4 a. u.

3. Theory

The renormalised-free-atom (RFA) model [20], which has been successful in the computation of Compton profiles of heavy transition metals and lanthanides (see e. g. [11 – 15, 20, 21]), was used to compute the Compton profile of Eu. In the RFA model, the atomic wave function is truncated at the Wigner-Seitz (WS) radius and renormalized to one per electron within the WS sphere to derive the approximate crystal wave function. In the case of Eu, it was found that 42.6% of the atomic 6s wave function [22] was inside the WS sphere, whereas the 4f wave functions were found to be almost confined within the sphere. We, therefore, ignored the renormalisation of the wave function of 4f-electrons and considered only the 6s-electrons in the present RFA scheme. The Compton profile $J_{6s}(p_z)$ due to 6s-electrons was calculated from the Fourier transform of the RFA wave function and an auxiliary function, which involves the reciprocal lattice vectors (K_n), the Fermi momentum (p_F), the number of points in the n^{th} shell, etc. The contribution of 25

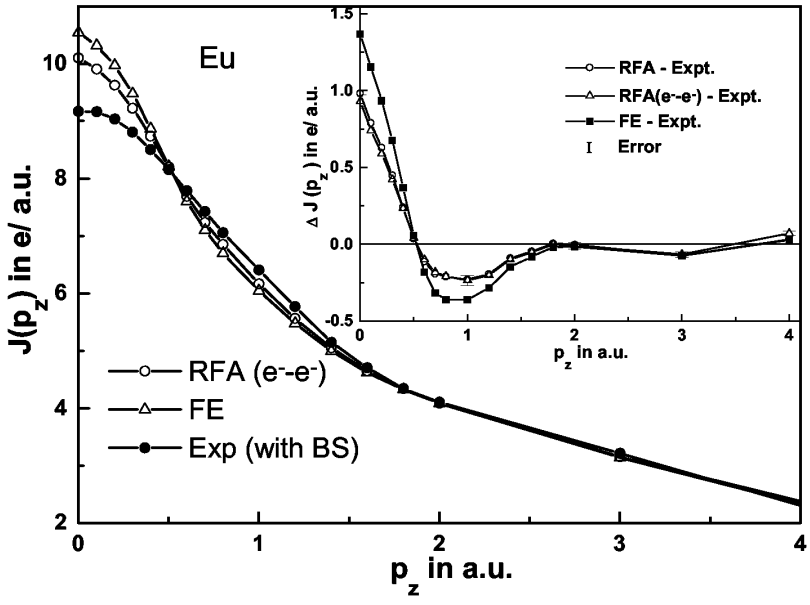

Fig. 1. Absolute experimental and convoluted theoretical Compton profiles of Eu. The differences between the convoluted theory and experiment are shown in the inset along with the statistical error $(\pm\sigma)$ in the experiment.

shells has been considered in the above summation to incorporate the crystalline effects in the bcc structure of Eu. It was observed that there was no significant change in the results if we used more K_n values. We have also computed the free electron theory (FE)-based Compton profile, using the formulae given in [15, 20], treating $6s^2$-electrons as free.

The total Compton profile for Eu is obtained by adding the free atom core contribution $[Xe]4f^7 5d^0$ from the tables of Biggs et al. [19] to the respective valence ($6s^2$) profile.

We have also incorporated the effect of the e^--e^- correlation in the RFA-based $J(p_z)$, using the approach of Das and Chaddah [23]. All the theoretical profiles so obtained were normalized in the same way as the experimental ones between 0 and 4.0 a. u.

4. Results and Discussion

Before comparing the theory with the experiment, the theoretical profiles were convoluted with the experimental resolution. The total profiles corresponding to the convoluted theory (the RFA model with e^--e^- correlation and the FE model) and experiment are shown in the main part of Fig. 1, while the difference profiles (convoluted theory-experiment) are shown in the inset, which shows that the inclusion of the electron-electron (e^--e^-) correlation in the RFA model slightly shifts the momentum density towards the higher momentum side about the p_F. This is expected because the e^--e^- interaction energy causes electrons to cross the Fermi surface. Figure 1 shows significant differences between the momentum density, particularly in the vicinity of $p_z = 0$, for both calculations and the experiment. The difference curves (inset) for the FE and the RFA models indicate that the simplistic assumption of a spherical Fermi surface in the FE or a crystalline environment approximation in the RFA calculation does not remain valid in the case of Eu. The large difference between the RFA model and the experiment may be due to the hybridization effects of s-, p-, d-, f-electrons, which are neglected in our RFA calculations. In fact, due to the non-availability of free atom wave functions for 5d- and 6p-electrons, we could not model these electrons within the RFA scheme and therefore computed the RFA Compton profile only for the $[Xe]4f^7 5d^0 6s^2$ electron configuration.

Table 1. Comparison of the full width at half maximum (FWHM) of the Compton profiles of different lanthanides measured by our group using a 20 Ci ^{137}Cs Compton spectrometer.

Element	FWHM in e/a. u.
Eu (this work)	3.47 ± 0.028
Tb [12]	3.62 ± 0.014
Ho [13]	3.56 ± 0.016
Yb [14]	3.44 ± 0.014

To compare the electronic properties of Eu with other representative lanthanides, namely, Tb ($Z = 65$), Ho ($Z = 67$) and Yb ($Z = 70$), in Table 1 we give the FWHM of Compton profiles of these lanthanides. It

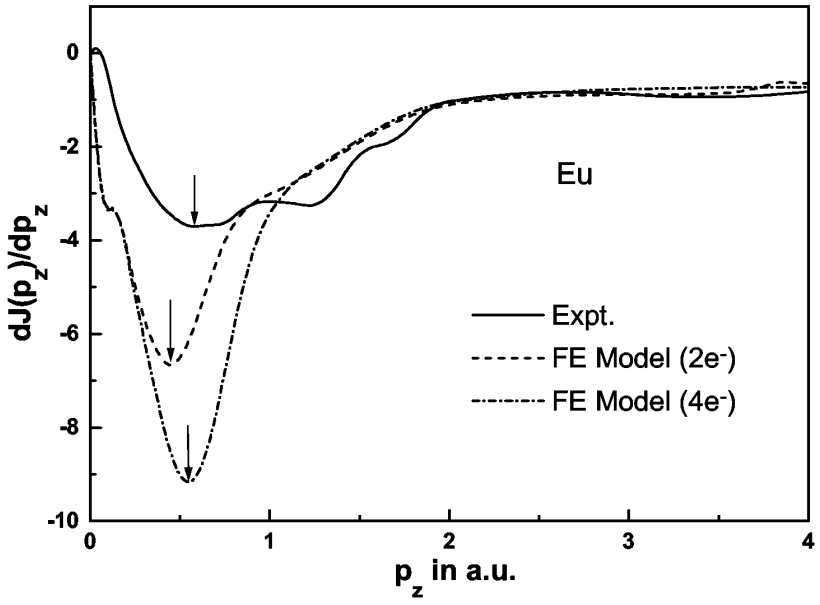

Fig. 2. The first derivatives of the experimental and convoluted free electron (FE) and Compton profiles. The FE model ($2\,e^-$) corresponds to [Xe]$4f^7$ treated within free atom and $6s^2$-electrons within free electron approximation, while the FE model ($4\,e^-$) is related to [Xe]$4f^5$ treated within free atom and $4f^2 6s^2$-electrons treated in hypothetical free electron approximation. Arrows denote the position of dips. See text for other details.

is seen from the table that the FWHM for half-filled Eu ($4f^7$) and full-filled Yb ($4f^{14}$) is lower than for the other two lanthanides. The lower value of the FWHM in case of Eu and Yb suggests that the 6s-electrons, which give sharper Compton line shapes in comparison to valence f-, d-, p-electrons, may contribute less in hybridization effects than the other two lanthanides.

In order to better identify the hybridization effects through Fermi surface related information, we have taken the first derivative $[\mathrm{d}J(p_z)/\mathrm{d}p_z]$ of the experimental Compton profile and the free electron model (computed for 2 and hypothetical 4 electrons) profiles. It is well established that in the case of a valence free electron profile (parabolic shape), the first minimum in the first derivative of the profile corresponds to p_F. The first derivatives of the experimental and both FE model profiles are shown in Figure 2. It is seen that the first minimum of the derivative curve corresponding to an FE model ($2\,e^-$)-based profile occurs at a lower momentum than that of the experimental curve. A reverse trend is seen for the hypothetical $4\,e^-$-based FE profile. The minima corresponding to $4\,e^-$-based FE model are closer to the experimental one. It shows the possibility of more than two electrons in the valence band, which may be due to hybridization in Eu.

In our earlier work [11, 13, 14], the use of Compton profiles to infer the cohesive energy of lanthanides has aroused considerable interest. The cohesive energy, consequent to the formation of a molecule or a solid, can be related to changes in $J(p_z)$. That is

$$E_\mathrm{coh} = \int_0^\infty p_z^2 [J_1(p_z) - J_2(p_z)]\mathrm{d}p_z, \qquad (3)$$

where J_1 and J_2 refer to the Compton profiles for the two states, namely solid and free atom, for which the energy of transformation is E_coh. The problems associated with deriving the cohesive energy from the experimentally determined Compton profile have been discussed by several workers (see, for example, [11, 13, 24]). Therefore we have calculated the cohesive energy using the RFA model, only. The numerical values of E_coh calculated by the RFA model (with and without e^--e^- correlation effect) comes out to be 2.31 eV and 2.22 eV, respectively. Delin et al. [6] have quoted the cohesive energy as 1.81 eV within the full-potential LMTO generalized gradient approximation (GGA), and 2.14 eV in the LDA. The good agreement between these results shows the importance of the RFA scheme in reproducing the cohesive property of lanthanides.

5. Conclusions

The measured Compton profile of polycrystalline europium has been interpreted in terms of a free electron-based profile and a renormalised-free-atom model. None of these models gives a reasonable agree-

ment with the present Compton measurements on Eu. Evidently there is a need of relativistic band structure calculations for analyzing the experimental Compton profile of Eu. Although the growth of large single crystals of Eu is extremely difficult, the measurement on single crystals may give more information about the Fermi surface topology.

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