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A Compton profile study of praseodymium and erbium

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Abstract : The Compton profiles and their first derivatives have been deduced from high energy Compton scattering measurements on polycrystalline praseodymium and erbium. The measurements at a resolution of 0.39 a.u. have been made using ^{137}Cs Compton spectrometer. In absence of band structure calculations, the data are compared with the renormalised-free-atom (RFA) and free electron models. The data are found to be in better agreement with the RFA predictions which include e^{-}-e^{-} correlation effect. An inspection of the first derivative of the Compton profiles reveals, quantitatively, the hybridisation in *s*-, *p*-, *d*- and *f*- electrons in both the lanthanides. In addition, the cohesive energy of both the lanthanides is also computed, and a comparison with the available data is made.

Keywords : Electron momentum density, Compton scattering, lanthanides, cohesive energy

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1. Introduction

An energy profile of Compton-scattered X-rays contains information about the electron momentum density, which is expressed as

$$J(p_z) = \iint n(p)dp_x dp_y, \qquad (1)$$

where $n(p)$ is the electron momentum density in the ground state. The above expression is valid within the impulse approximation, which requires the energy transferred to the electron to be much greater than its binding energy; its final state is then treated as a plane wave like. The *z*-axis momentum component of the electron in its ground state, p_z, can be related by simple kinematics to the energy of incident and scattered photons; and also the angle of scattering. Therefore, the Compton spectroscopy has been widely applied to various kinds of materials in order to study their electronic structure and bonding mechanism in momentum space (see for example, Ref. [1]). In such studies, electron

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momentum is normally expressed in atomic units (a.u.) where $e = m = \hbar = 1$, $c = 137$, then one a.u. of momentum = 1.99×10^{-24} kgms^{-1}.

Praseodymium (Pr) and erbium (Er) are the rare-earth metals with a variety of unusual magnetic structures (see, for example, Refs. [2-10]). The electronic structure emerging from various experimental and theoretical investigations (see, for example, Refs. [11-18]) is that of an f-band complex which splits into an occupied and unoccupied part, with the unoccupied part well separated from the Fermi level. Regarding Compton profile studies on Pr, Varghese *et al* [19] have reported the Compton profile of Pr using 59.54 keV γ-rays from 300 mCi ^{241}Am source. The scattered radiations have been detected using a coaxial germanium detector. As discussed in our earlier work on Sm and Yb [20,21], the measurement on Pr using ^{241}Am source may also have the following problems:

(i) overlapping of fluorescence lines of Pr$(K_\alpha = 36.03keV, K_\beta = 40.75keV)$ with the energy tail of Compton profile leading to uncertainties in instrumental resolution correction.

(ii) poor resolution (Gaussian FWHM of 0.8 a.u.) due to use of a co-axial germanium detector for 40-60 keV radiations.

In the present paper, we present an accurate isotropic Compton profile of Pr and a first ever line profile of Er using our 20 Ci ^{137}Cs Compton spectrometer. Due to difficulties (like requirement of ultra high vacuum conditions and very high chemical reactivity of both the lanthanides) in growing large size single crystals (15 mm dia and 3-5 mm thickness), we have decided to undertake the measurements on polycrystalline samples. In the absence of band calculations, we have analysed the isotropic profiles using the renormalised-free-atom (RFA) and free-electron (FE) models. The first derivative of the experimental Compton profiles is interpreted in terms of the hybridisation effect of spd-f orbitals. From our RFA data, we have also derived the cohesive energy of both the lanthanides.

2. Experiment

The Compton profile measurements on Pr and Er were carried out using a 740 GBq (20 Ci) ^{137}Cs Compton spectrometer [22,23] which is equipped with a high purity Ge detector. Both the samples were kept in a circular ampoule with mylar windows on both the front and the back side. The sample ampoule was held vertically and the γ-rays (662 keV) were allowed to fall normally on it. The incident radiations were scattered by the sample through a mean angle of 160°±0.6°. The experimental parameters along with other details of data are given in Table1. The raw Compton data were accumulated by a 4096 channel analyzer (Canberra, Accuspec B) with a channel width of about 0.035 a.u. In order to avoid electronic drift in the amplification and analogue-to-digital conversion, the electronics was kept at an ambient temperature (21°C). During the measurements, the stability of the detection system was checked from time to time and was observed to be smaller than one channel. The overall momentum resolution of the spectrometer used by us is 0.39 a.u., which is better than the conventional ^{241}Am Compton spectrometers (0.60 a.u.). The data were corrected for background (measured without sample), deconvolution, energy dependent

Table 1. Experimental parameters for the Compton line shape measurements of Pr and Er.

Target	Sample dimensions	Exposure time (hrs.)	Integrated counts (-10 to +10 a.u.)	Multiple scattering	Integrated BS contribution (-6 to +6 a.u.)	Normalisation of profile (0 to 6.0 a.u.)
Pr	sample dia = 1.60cm, thickness = 0.40 cm, bulk density = 2.75 g/cm^3	255	3.4 x 10^7	8.94%	0.18e$^-$	21.70e$^-$
Er	Sample dia = 1.50 cm thickness = 0.35 cm, bulk density = 2.90 g/cm^3	341	2.5x10^7	8.52%	0.39e$^-$	24.22e$^-$

corrections like detector efficiency, photon absorption and Compton cross section. The line shape was transformed from energy to momentum scale, and the profile was normalised to free atom area. These corrections were made using the computer code of Warwick group [24]. The deconvolution (instrumental resolution correction) was limited to stripping off the low energy tail from the data, therefore the theoretical profile has to be convoluted with experimental resolution. We have also incorporated the correction upto triple scattering by using a Monte Carlo scheme of the same group [25]. In the Monte Carlo simulation, the ratio of the number of multiple scattering events in the Compton profile to the total number of scattering events depends upon photon energy, sample material, sample dimensions and geometry of the spectrometer. The ratio of multiple to single scattering events in both the lanthanides is given in Table 1. Moreover, following the approach of Mathur and Ahuja [26], the experimental profiles were also corrected for the effect of bremsstrahlung (BS) contribution due to photo and Compton recoiled electrons liberated in the samples.

3. Theory

Since the band structure based Compton profiles for both the lanthanides are not available, we have used the RFA model [27], which was found to be successful in the computation of momentum densities of other lanthanides. The model is based on an approach that the atom in a solid is not free but confines to its Wigner-Seitz(WS) cell. The calculation begins from the free-atom Hartree-Fock atomic wave function, which is truncated at the WS radius and renormalised to one per electron (within the WS sphere) to conserve the charge neutrality. In this way the solid is constructed from individual atoms. In the case of Pr and Er, using the 6s free atom wave functions of Herman and Skillman[28], it was found that 38.2% and 36.7% respectively of the wave functions were inside the WS spheres. It was

in contrast to the 4*f* wave functions which were almost confined within the respective spheres. Therefore, 4*f* electrons were not considered in the RFA scheme whereas the renormalisation was expected to be significant for the valence *6s* electron only since their wave function is quite extended. Therefore, only *6s* electrons were considered in the present RFA scheme. In Figure1, we have plotted the free atom (FA) and the RFA wave functions $[\phi_{6s}(r)]$. For the hcp structure, the electron momentum density $n(p)$ corresponding to the *6s* band can be computed using the following relation [27]

$$n(p) = 2 \sum_{|p-K| \le p_F} \left|\phi^{(c)}(K_n)\right|^2 < 1 + \cos K_n . \tau > /2 \quad (2)$$

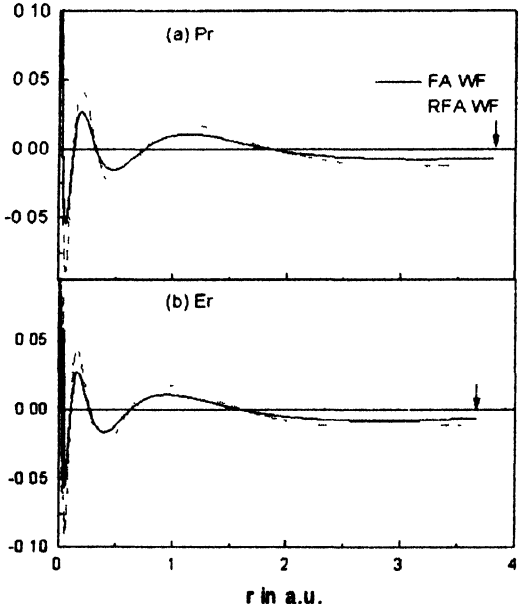

Figure 1. Free atom (FA) 6s wave function (WF) before and after truncation and renormalisation (RFA) to one within the Wigner-Seitz (WS) sphere for (a) Pr and (b) Er. The vertical down ward arrow shows the respective radius for the WS sphere.

Here, p_F is the Fermi momentum and τ determines the position of an atom in the unit cell. In the present RFA calculations, 25 shortest reciprocal lattice vectors (K_n) were considered to incorporate the crystalline effects. We have also computed the free electron (FE) theory based Compton profiles using the formulae given in Ref.[29] treating $6s^2$ electrons as free.

The total theoretical profiles corresponding to all electrons were obtained by adding the free atom core contribution $[Xe]5d^0 4f^3$ for Pr and $[Xe]5d^0 4f^{12}$ for Er from the tables of Biggs *et al* [30] to the respective $6s^2$ electron profile. The effect of the $e^- \text{-} e^-$ correlation, which shifts the $n(p)$ from below the p_F to above p_F was also incorporated in the RFA model

Table 2. The theoretical (unconvoluted) and experimental Compton profiles (e/a.u.) of Pr and Er. The experimental Compton profiles for Pr and Er are given in columns 5 and 9, respectively. After 6.0 a.u., the experimental data in such measurements (dominated by core electrons) show poor statistics, therefore the profiles are listed only upto 6.0 a.u. Statistical error ($\pm\sigma$) is given at few points.

p_z	$J(p_z)$							
	Pr.				Er.			
a.u.	FE	RFA	RFA(e-e)	Expt.	FE	RFA	RFA(e-e)	Expt.
0.00	10.565	10.026	9.982	9.708±0.019	10.135	9.925	9.878	9.17±0.021
0.10	10.546	10.011	9.966	9.633	10.042	9.820	9.773	9.154
0.20	10.269	9.813	9.769	9.487	9.815	9.634	9.588	9.053
0.30	9.852	9.450	9.414	9.268	9.488	9.286	9.246	8.869
0.40	9.247	9.037	9.018	8.970	9.007	8.912	8.887	8.602
0.50	8.460	8.356	8.373	8.593	8.377	8.254	8.262	8.275
0.60	7.504	7.701	7.784	8.156	7.609	7.657	7.724	7.921
0.70	6.923	7.191	7.037	7.685	6.996	7.097	7.178	7.558
0.80	6.555	6.809	6.747	7.207	6.748	6.844	6.860	7.194
1.00	5.821	6.027	6.027	6.282±0.014	6.208	6.293	6.293	6.501±0.016
1.20	5.190	5.337	5.337	5.479	5.678	5.749	5.749	5.940
1.40	4.701	4.790	4.790	4.825	5.222	5.276	5.276	5.442
1.60	4.340	4.384	4.384	4.328	4.846	4.884	4.884	4.982
1.80	4.062	4.087	4.087	3.939	4.552	4.578	4.578	4.633
2.00	3.833	3.853	3.853	3.676±0.009	4.315	4.333	4.333	4.396±0.013
3.00	2.846	2.851	2.851	2.763±0.007	3.436	3.441	3.441	3.387±0.01
4.00	1.989	1.989	1.989	2.037±0.006	2.618	2.618	2.618	2.621±0.008
5.00	1.449	1.449	1.449	1.482±0.004	1.939	1.939	1.939	1.940±0.006
6.00	1.139	1.139	1.139	1.159±0.003	1.470	1.470	1.470	1.476±0.005

profiles using the methodology of Das and Chaddah [31]. The total theoretical profiles were normalised to number of electrons as given in Table 1.

4. Results and discussion

In Table 2, we have listed the duly corrected experimental Compton profiles of Pr and Er together with the theoretical Compton profiles (unconvoluted) derived from the FE and the RFA (with and without incorporating the $e^- - e^-$ correlation effect) models. In the table, we have given the high energy side experimental Compton profiles. It is worthwhile to mention that in such a high energy Compton profile measurements, the low energy side of profile

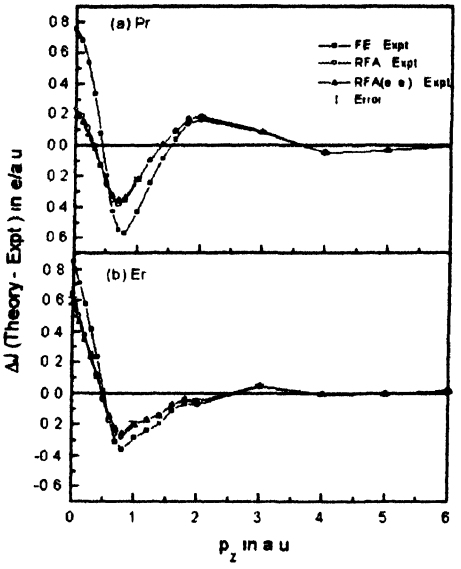

Figure 2. Difference (ΔJ) between the experimental and theoretical profiles for (i) free electron model (ii) RFA model and (iii) RFA with e-e correlation correction. The theory has been convoluted with the instrumental function (Gaussian shape of FWHM 0.39 a.u.).

is discarded because of the asymmetric broadening which arises from the detector response function, multiple scattering correction and source broadening due to small-angle Compton scattering in the ^{137}Cs source. All these effects are dominated in the low energy side of the profile, but in any event the high energy side of the Compton peak appears to be cleaner. All theoretical and experimental values of $P_r(Z = 59)$ at $p_z = 0$ are found to be higher than the respective values for $Er(Z = 68)$. For an overall comparison, all the theoretical profiles were convoluted with the instrumental function (Gaussian FWHM of 0.39 a.u.) of the experiment. Figure 2 shows the difference (ΔJ)between the convoluted theoretical and the experimental profiles for both the lanthanides. It is seen that the FE model based profiles give a poor agreement with the experiment for both the lanthanides, which is understandable in terms of unrealistic assumptions of FE theory in case of such heavy elements. In both the ΔJ curves, it is seen that the RFA model profile with e^--e^- correlation gives a better agreement with the respective measurement, although near $p_z = 0$ the RFA calculations (with and without correlation effect) overestimate the momentum density. Large differences between the simple RFA model and the Compton measurements may be due to negligence of hybridisation effects of *s*-, *p*-, *d*-, *f*- electrons in our RFA calculations. In fact, due to the non-availability of free atom wave functions for 6*p* and 5*d* electrons and limitations in the truncation of 4*f* electrons, we could not model these electrons within the RFA scheme. We believe that the Compton profiles corresponding to 5*d* and 6*p* electrons of both the lanthanides are expected to be flatter than the corresponding 6s electrons. Therefore, a reasonable incorporation of 6p or 5*d* electrons in

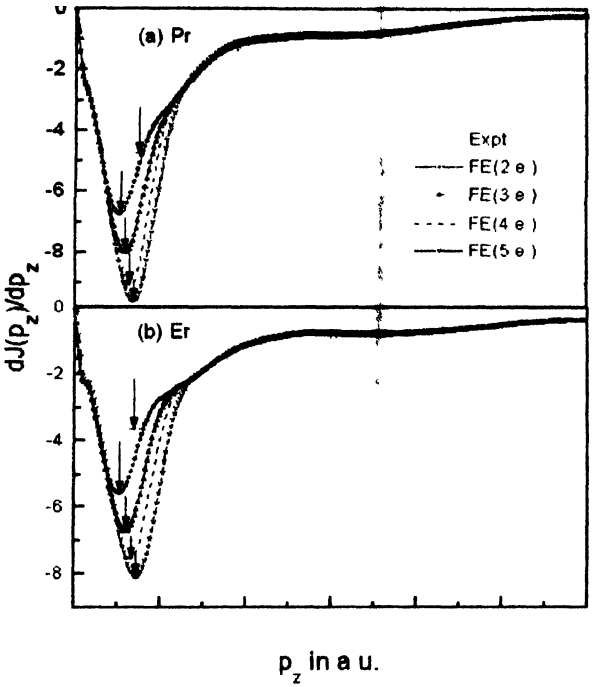

Figure 3. The first derivatives of the convoluted free electron (FE) and experimental Compton profiles for (a) Pr and (b) Er. In case of Pr, [Xe]$4f^{3-n}$ and $5d^n$-$6s^2$ (n=0,1,2,3) are taken as core and valence band electrons, respectively; while for Er the respective configurations are [Xe]$4f^{12-n}$ and $5d^n$-$6s^2$. In bracket the number of electrons corresponds to the valence band electrons only.

the evaluation of total theoretical Compton profile will reduce the magnitude of the absolute theoretical profile in the low momentum region. It is then expected to lead to a better agreement between the theoretical and the experimental momentum densities. To extract a very unique information on the hybridisation effects, we have taken the first derivative $(dJ(p_z)/dp_z)$ of the experimental Compton profiles as well as the FE model profiles computed for hypothetical 2 to 5 electrons for Pr and 2 to 7 electrons for Er. The position of negative peak in the first derivative corresponds to the Fermi surface aspects, which defines the region of variation of $n(p)$separating filled and empty states. It may be noted that in the case of a FE profile for valence electrons (inverted parabolic), the minimum in the first derivative of the profile corresponds to p_F. The derivatives of the absolute experimental and the FE model profiles (for 2 to 5 electrons) for Pr and Er are shown in Figures 3(a) and (b) respectively. The appearance of ripples in the momentum region 1-3 a.u., is an inevitable artifact, of the differentiation of data containing experimental errors. It is seen that a sharp dip in both the derivatives corresponding to hypothetical 5 electrons based FE model profile occurs near smoother dip of the respective experimental curves. This indicates a possibility of nearly five electrons in the valence band of both the rare earths, which may be ascribed to the *spd-f* hybridisation effects. Therefore, the present

Table 3. Cohesive energy (E_{coh}) in eV for Pr and Er along with the results of other investigations

Sample	Our RFA	LMTO [17]		Johansson and Munck
		(a) GGA	(b) LDA	[18]
Pr	4 65	4.55	5.13	4.60
Er	3.45	4.42	4.95	4.51

data, within the limitation of free electron theory, suggests the valence band configuration as $(4f\ 5d\ 6s\ 6p)^5$ for both the lanthanides. Using RFA Compton profiles, we have also computed the cohesive energy, E_{coh}, defined as the difference between the bulk and the total atomic energies, of both the lanthanides. In our earlier work on lanthanides [see, for example, 21, 29] the computation of cohesive energy using RFA model was found to be in reasonable agreement with the band structure calculations. E_{coh} can be calculated from the Compton profiles by using the formula given below [32]:

$$E_{coh} = \int_0^{p_{max}} \Delta J_{S,FA} p^2 dp, \tag{3}$$

where $\Delta J_{S,FA}$ refers to the difference in Compton profiles for the two states namely solid (J_s) and free atom (J_{FA}), respectively. The value of J_s was taken from the present RFA computations and those for (J_{FA}) from the tables of Hartree-Fock free atom Compton profile [30]. As reported by several workers (see, for example, Refs. [32, 33]), the E_{coh} derived from the experimental Compton profile may lead to wrong results due to the weighting of p^2 [in eq.(3)], particularly in the high momentum region. Therefore, we have used only the RFA profiles, which differ from the free atom profile upto 2.0 a.u. or so, for the computation of cohesive energy of both the lanthanides. In Table 3, we give the RFA based E_{coh} (with p_{max} = 2 a.u.) along with the available data on E_{coh} computed from the full-potential (FP) linear muffin tin orbital (LMTO) with local-density-approximation (LDA) and the generalised-gradient-approximation (GGA) [17]. The RFA based cohesive energy of Er is found to be smaller than the available data [17, 18], while for Pr our RFA values are closer to the interpolation data of Johansson and Munck [18].

5. Conclusions

In the present paper, we have presented the isotropic experimental Compton profiles of praseodymium and erbium and compared these profiles with free electron and renormalised-free-atom (with and without $e^- \text{-} e^-$ correlation) models. None of the models give reasonable agreement with the experimental line shapes. The first derivatives of both the Compton profiles suggest the hybridisation effects of *s*-,*p*-,*d*- and *f*- electrons. The computed cohesive energy of praseodymium is in agreement with the available data whereas that of erbium is smaller than it. This work confirms the efficiency of Compton spectroscopy in the study of electronic structure of lanthanides. To study all the features of our Compton measurements, accurate band structure based momentum densities are urgently required.

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