Electronic structure study of Gd_2O_3: A Compton scattering study

F.M.Mohammad[1], A.M.Ghaleb[2], S.Jagrati[3], K.C.Bhamu[3], B.L.Ahuja[3]

[1]*Department of Physics, College of Science, University of Tikreet, Tikreet, Iraq*

[2]*Department of Physics, College of Science, University of Kirkuk, Kirkuk , Iraq*

[3]*Department of Physics, University College of Science, M.L. Sukhadia University, Udaipur, 313001 Rajasthan, India*

Mail:dr_Farid2006@yahoo.com.

Abstract:

The isotropic Compton profile of Gd_2O_3 have been measurea using 661.65 keV γ-radiations emitted from our 740 GBq (20 Ci) ^{137}Cs Compton spectrometer at an intermediate resolution of 0.34 a.u. The experimental Compton profiles have been compared with the theoretical Compton profiles deduced from the linear combination of atomic orbitals (LCAO) method as embodied in CRYSTAL09 code, and also compared with ionic model. The measurement is compared with (LCAO) calculation within approximation (HF) and DFT (LDA, GGA, SOGGA),it is show that the (HF) is in agreement with experimental data. The ionic model calculations for a number of configurations of $Gd_2^{+x}O_3^{-x}$ ($0.0 \leq x \leq 6$) have also been performed while taking free atom profiles and the model suggests transfer of 5.0 electrons from the valence 5d shell or 6s shell for Gd to the 2p shell of O.

Keywords : X-ray scattering, Band structure calculations, Density functional theory, ionic model.

Introduction:

The rare earth sesquioxides (RE_2O_3, RE = rare earth element) are transparent in visible region and have wide band gap [1]. In RE_2O_3 each rare earth atom donates its three electrons to the highly electronegative oxygen atom, leaving the more localization of the remaining 4f electrons at the rare earth site. RE_2O_3 have their importance as catalysis, high temperature materials, optical material, electronic industries, nuclear engineering, chemicals, biomaterials, processing of the ceramics as additives for low temperature sintering, as grain growth inhibitors, phase stabilizers etc. [2-3]. RE_2O_3 are found in three different polymorphic forms. Light lanthanides have A type (hexagonal) structure, heavy lanthanides crystallize in C type (cubic) structure and the middle lanthanides are found either in C type or in B type (monoclinic) structure. Gadolinium oxide (Gd_2O_3), middle rare earth sesquioxide, has been extensively used in different applications [4]. At room temperature Gd_2O_3 crystallize in cubic structure, while phase transformation from cubic to monoclinic takes place at 1200ºC. To our knowledge there have been very few studies on the electronic structure properties of Gd_2O_3. Hussein [5] has synthesized Gd_2O_3 compound using thermal decomposition process and examined the acidity of the surface and tested the catalytic activity of Gd_2O_3. Using x-ray powder diffraction technique and Rietveld refinement analysis, Pires et al [4] have done the structural characterization of Gd_2O_3 and Gd_2O_3:Eu^{3+}. Hirosaki et al [6] have computed the equilibrium lattice dimensions for cubic Gd_2O_3, along with most of the rare earth sesquioxides of A and C type structure, using density functional theory (DFT). Petit et al [7] have used the self interaction corrected local spin density method to investigate the electronic structure of rare earth dioxides and rare earth sesquioxides. Authors found that for most of the sesquioxides, including Gd based sesquioxide, trivalent ground state configuration is most favorable. Zhang et al [3] have studied the irreversible phase transition in Gd_2O_3 from cubic to hexagonal phase at high pressure. The authors have also determined the compressibility and bond distances in both the phases by the refinement of the x-ray diffraction data.

Compton scattering is a versatile tool to probe the electronic properties of the material. In Compton scattering one measures the Compton profile (CP), $J(p_z)$, which is the projection of electron momentum density along the scattering direction. Within the impulse approximation (IA) one can define the CP as,

$$J(\vec{p}_z) = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho(\vec{p})dp_x dp_y \quad \text{.....(1)}$$

Where n(**p**) is the electron momentum density of the electrons of the sample and is related to the real space wave function of the electrons. Mathematically,

$$\rho(\vec{p}) \propto \sum_i \left| \int \Psi_i(\vec{r}) \exp(-i\vec{p}.\vec{r}d\vec{r}) \right|^2 \quad \text{.....(2}$$

Here Ψ(r) is the electron wave function in real space and the summation is taken over all the occupied states.

It may be noted that in comparison to other rival spectroscopy techniques used in determination of electronic structure of materials, the Compton scattering has particular advantages [8,9]. This technique does not require the long electron mean free path as in the case of de Hass-van Alphen experiment. Therefore, applicability of Compton scattering is not limited to the systems with low defect and/or impurity concentrations. Also, Compton scattering does not suffer from the drawbacks like surface sensitivity in case of photoemission or electron scattering experiments since no charged particles entering or leaving the sample are involved. The present work aims to the first ever Compton profile measurements of Gd_2O_3 using 661.65 keV γ-

radiations. To compare our experimental data we have computed the theoretical CPs, energy bands and density of states using CRYSTAL09 code.

Experiment:

We have measured the Compton profile of Gd_2O_3 using 740 GBq (20 Ci) ^{137}Cs Compton spectrometer [10]. Due to the non-availability of large size (diameter 13 mm and thickness 3 mm) single crystals, we have measured the isotropic CPs of Gd_2O_3. The high purity (99.9 %) sample in the form of pellet (thickness 5.04 mm and diameter 24 mm) was used as the target. The incident γ-radiation of energy 661.65 keV were scattered by the sample at an angle of 160 ± 0.6º. The scattered radiations from the sample were detected by a high purity germanium detector (Canberra, model GL0510P) and associated electronics like spectroscopy amplifier, analog to digital convertor, multichannel analyzer, etc. The overall resolution of the spectrometer was 0.34 a.u. Using ^{57}Co and ^{133}Ba γ-ray sources, the electronic drift was monitored several times during the measurements and was found to be negligible. The sample was exposed for 146 h to get an integrated intensity of 1.4 x 10^7 counts at Compton peak. To extract the true CP from the raw data, raw data was corrected for several systematic corrections like background, instrumental resolution (limited to stripping off the low energy tail), detector efficiency, Compton cross-section and absorption correction, etc. using the prescription of Warwick group [11]. The raw data was corrected for background by subtracting background from the raw data. For this background was separately measured for 4 days, after removing the sample from the sample holder. Then Monte Carlo simulation [12] was used for the removal of the multiple scattering effects from the data. The effect of multiple scattering within the momentum range 0-10 a.u. was found to be 6.4%. Finally, experimental profile was normalized to the free atom area (momentum range 0-7 a.u.) viz. 60.30 e^- [13].

Calculation:

a) LCAO Calculation:

To interpret our experimental Compton data we have computed CPs, of Gd_2O_3 using the CRYSTAL09 [14, 15] code of the Torino group. This code is based on the linear combination of atomic orbital's (LCAO). In this approach crystalline orbital's are expanded over the basis sets of the atomic orbital's. This code includes the (HF) approximation and density functional theory (DFT) within the local spin density approximation (LDA), generalized gradient approximation (GGA) and second order generalized gradient approximation (SOGGA).

b) Ionic model:

The theoretical Compton profiles of Gd_2O_3 for different ionic configuration were calculated from the free atom profiles of Gd and O as taken from Biggs et al.[13].The valence profiles were added to core contribution to get the total profiles and then normalized to 60.30 electrons in the range 0 to +7 a.u.

Results and discussion:

The raw Compton spectrum for polycrystalline Gd_2O_3 is shown in Fig (1) All the theoretical values given in the Fig (2.a) have been convoluted with the residual instrumental function (RIF) of the spectrometer section (2) and are normalized to an area of 60.292 electrons being the number of electrons from 0 to 7 a.u. in the Free atom profile. The experimental values before and after double scattering correction were also normalized to this area .Also Fig (2.b)show the difference between all theoretical using (LCAO),with experimental after convoluted with the instrumental function of the experiment viz 0.34a.u.(Gaussian FWHM)in the present case. As well as the table (1) give compared theoretical value by using (LCAO) method after being convoluted with (RIF),that it can be seen the (HF) calculation agreement with experimental but other determine using (LDA,GGA and SOGGA) are mostly than with experiment.

In Figure (3.a), we compare the values given above upto 7 a.u. It is seen that for p_z between 0 to 0.2 a.u. more theoretical values ($Gd_2^{+1}O_3^{-1}$ to $Gd_2^{+5}O_3^{-5}$) are higher than experiment but for 0.4 to 1.4 a.u. the experimental values are higher than theory. The nature of all the curves as similar beyond 1.8 a.u. and all values are close to experiment.

It is clearly seen that the free atom values differ appreciably than the ionic models .In Fig (3.b) we plot the difference ΔJ (Theory – experiment) for the values obtained in ionic models (cols 2 to cols 6) which correspond to Gd_2O_3,as follows in table(2) .It is seen that upto nearly 0.3 a.u.,the difference are positive which means that theoretical values are larger than the experiment. Between 0.4 to 1.4 a.u.,the experimental values become larger. For O^{-5} model, the difference are initially negative. After 2 a.u. difference are very small, the theoretical and experimental values agree very well. As pointed above for the ionic models the difference are much smaller than the free atom model (not shown) Also, it can be seen that effect of varying charges on Gd and O is visible only upto 1.8 a.u.Beyond 1.8 a.u.,all configuration show indentical behavior and are overlapping with each other .Moreover, the differences are within the experimental error such an agreement among various difference profiles at higher momentum (> 4 a.u.)is expected because the contribution in this momentum region is mostly due to inner electron ,which remain unaffected in the compound formation , Fig(3.b) show that the $Gd_2^{+5}O_3^{-5}$ configuration gives the best agreement among the ionic arrangements. Thus, the simple model suggests that in this compound five electrons are transferred from 5d&6s orbital of Gd to 2p orbital of O and hence the bonding in Gd_2O_3 is primarily ionic.

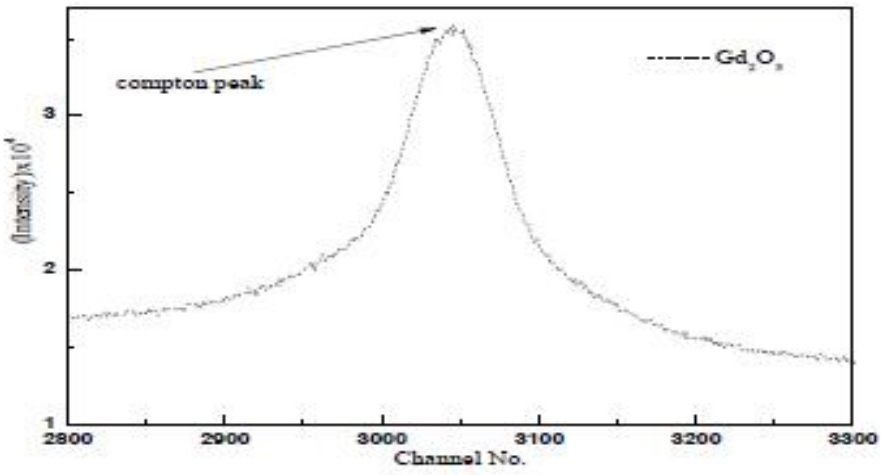

Fig .1. Raw experimental data for polycrystalline Gd_2O_3.

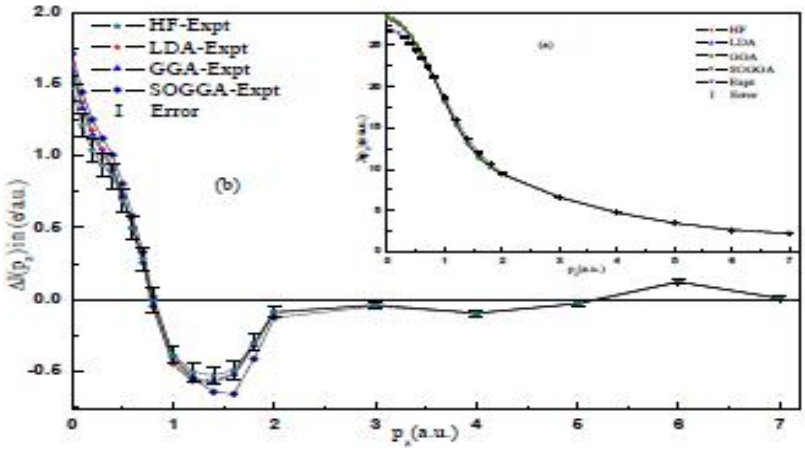

Fig.2:(a):comparison of theoretical and experimental Compton profiles for Gd_2O_3. (b): difference between theoretical and experimental Compton profiles Of polycrystalline Gd_2O_3 .The statistical error is shown for some points. Theory has been convoluted with the (RIF) .

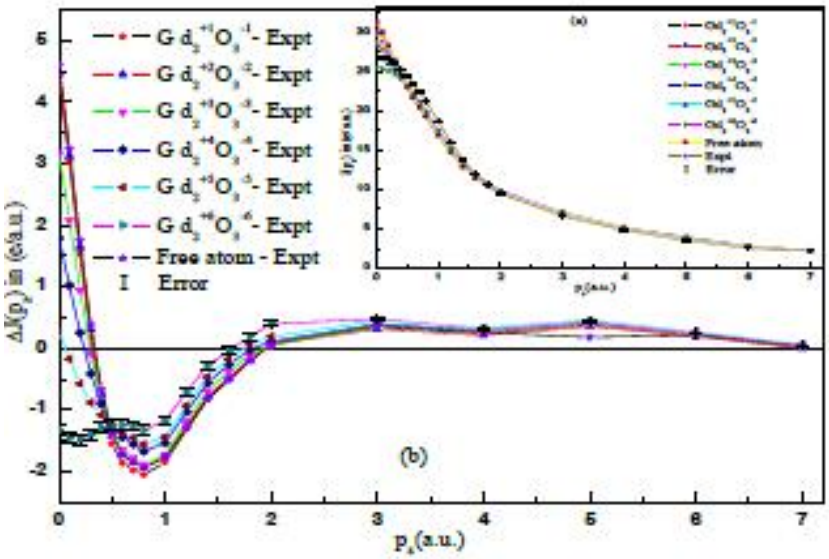

Fig.3:(a):Comparison of theoretical values using ionic model and experimental Compton profiles for Gd_2O_3.(b):difference between theoretical and experimental Compton profiles Of polycrystalline Gd_2O_3 .The statistical error is shown for some points. Theory has been convoluted with the (RIF) .

In table (3) also we present compared the HF Compton profiles along with the experiment and the Compton profile for $Gd_2^{+5}O_3^{-5}$ configuration, which showed best agreement with the data. We have,

again, plotted the Compton profiles between theory and experiment in Fig (4) Compton profiles convoluted with the Gaussian of 0.34 a.u. FWHM. When we compare our measurement with calculated profiles, it can be seen that at p_z=0 the Compton profile is less than that for the ionic model and HF .In the low momentum region $p_z = 0 \ to \ 0.3 \ a.u.$the ionic model shows agreement than the HF whereas in the momentum region $p_z = 0.4 \ to \ 1.2 \ a.u.$ better agreement was found by HF, but from $p_z = 1.2 \ to \ 1.8 \ a.u.$ ionic model give better with experimental results. Beyond 2 a.u., the (HF) agreement with experiment. At the table (3) shows also compare between our theoretical (HF and $Gd_2^{+5}O_3^{-5}$) in the low momentum region $p_z = 0 \ to \ 1.2 \ a.u.$ the HF Compton profiles are larger than the ionic model ($Gd_2^{+5}O_3^{-5}$) but in the momentum region $p_z = 1.2 \ to \ 7 \ a.u.$ the HF less than from ionic model.

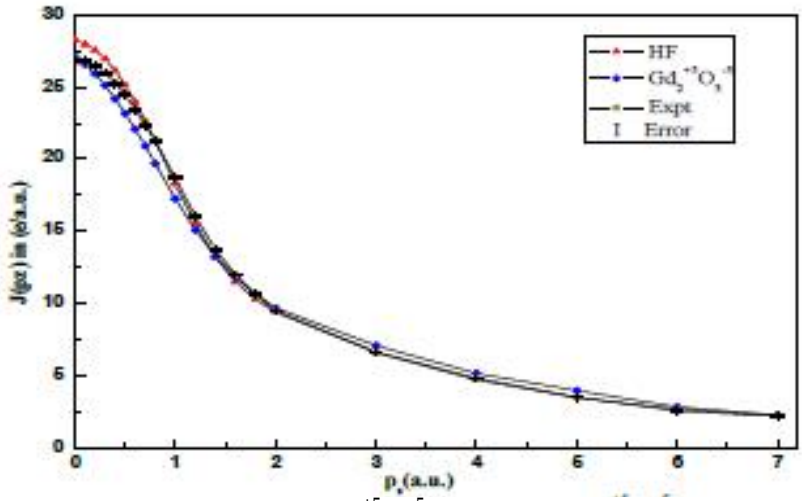

Fig .4: Comparison of theoretical (HF and $Gd_2^{+5}O_3^{-5}$) and experimental Compton profiles for Gd_2O_3.

Conclusion:

Using 661.65 keV 20 Ci ^{137}Cs Compton spectrometer. In case of Gd_2O_3 the first ever isotropic experimental Compton profiles are compared with (LCAO) calculation .None of the approximation (HF) give reasonable agreement with the experimental line shapes. We have also computed Compton profile by ionic model; these results have been compared with experimental data and free atom, whereas choosing full as well as partial ionicity. Our measurements clearly favour d^1 type distribution i.e. complete transfer of valence electrons to oxygen atoms. The ionic model calculations for a number of configurations of Gd_2^{+x} O_3^{-x} $0 \leq x \leq 6$ suggest transfer of 5 electrons from the valence ($5d^16s^2$) state of Gd to the $2p^2$state of O.

Table .1: Our theoretical compared with experimental Compton profiles for Gd_2O_3. All the quantities in atomic. The profiles are normalized so that the integral from 0 to 7.0 a.u. is 60.30 electrons. All theoretical values have been convoluted with the residual instrumental function (RIF).

P_z(a.u)	LCAO Calculations J(P_z) (e/a.u.)				Experimental J(P_z) (e/a.u.)	
	HF	LDA	GGA	SOGGA	Before DS	After DS
0	28.2558	28.429	28.38329	28.50091	26.089	26.78819±0.082
0.1	27.95897	28.11942	28.07786	28.19251	26.055	26.74806
0.2	27.54049	27.67885	27.64294	27.75344	26.029	26.50109
0.3	26.9335	27.04127	27.01286	27.11762	25.700	25.99456
0.4	26.1193	26.19022	26.17076	26.26825	24.736	25.26179
0.5	25.11384	25.14683	25.13678	25.22588	23.956	24.42134
0.6	23.94498	23.94373	23.94259	24.02255	23.161	23.44132
0.7	22.64312	22.61419	22.62077	22.6911	21.801	22.36271

0.8	21.24145	21.19258	21.20526	21.26565	20.992	21.24826
1	18.30199	18.23554	18.25483	18.2945	18.404	18.69124±0.06
1.2	15.50583	15.44335	15.46198	15.46436	15.695	16.01734
1.4	13.19481	13.14556	13.15883	13.07943	13.391	13.72486
1.6	11.49125	11.45715	11.46489	11.32509	11.980	11.98504
1.8	10.29037	10.26981	10.27422	10.17696	10.426	10.59285
2	9.40614	9.39543	9.39807	9.36064	9.3381	9.4897±0.038
3	6.59164	6.5965	6.59588	6.58664	6.7239	6.63459±0.028
4	4.72422	4.724	4.7239	4.72148	4.8751	4.81982±0.021
5	3.47313	3.47129	3.47139	3.46866	3.5688	3.50153±0.016
6	2.6848	2.68344	2.68353	2.68162	2.6666	2.56139±0.012
7	2.21625	2.21537	2.21543	2.21374	2.3708	2.20918±0.010

Table .2: Our theoretical compared with experimental Compton profiles for Gd_2O_3. All the quantities in atomic. The profiles are normalized so that the integral from 0 to 7.0 a.u. is 60.30 electrons. All theoretical values have been convoluted with the residual instrumental function (RIF).

p_z (a.u.)	Ionic Model $J(P_z)$ (e/a.u.)						Experimental $J(P_z)$ (e/a.u.)	
	$Gd_2^{+1}O_3^{-1}$	$Gd_2^{+2}O_3^{-2}$	$Gd_2^{+3}O_3^{-3}$	$Gd_2^{+4}O_3^{-4}$	$Gd_2^{+5}O_3^{-5}$	$Gd_2^{+6}O_3^{-6}$	Before DS	After DS
0	31.1717	31.2623	29.9482	28.5735	27.0720	25.4632	26.089	26.78819±0.082
0.1	29.7608	29.8621	28.8298	27.7664	26.5730	25.2867	26.055	26.74806
0.2	28.0266	28.1401	27.4424	26.7497	25.9239	25.0241	26.029	26.50109
0.3	26.1637	26.2884	25.9127	25.5803	25.1122	24.5942	25.700	25.99456
0.4	24.3861	24.5186	24.3982	24.3555	24.1763	23.9746	24.736	25.26179
0.5	22.8693	23.0038	23.0325	23.1649	23.1629	23.1679	23.956	24.42134
0.6	21.5739	21.7050	21.7883	21.9972	22.0769	22.1987	23.161	23.44132
0.7	20.3773	20.5008	20.5787	20.8056	20.9113	21.1025	21.801	22.36271
0.8	19.1948	19.3078	19.3580	19.5772	19.6855	19.9229	20.992	21.24826
1	16.8427	16.9306	16.9638	17.1514	17.2529	17.5115	18.404	18.69124±0.06
1.2	14.6991	14.761	14.8248	14.9833	15.0820	15.3048	15.695	16.01734
1.4	12.9019	12.9397	13.0320	13.1637	13.2600	13.4384	13.391	13.72486
1.6	11.4817	11.4990	11.6099	11.7166	11.8084	11.9427	11.980	11.98504
1.8	10.3969	10.3976	10.4819	10.5662	10.6519	10.7830	10.426	10.59285
2	9.5671	9.55454	9.53466	9.59993	9.67893	9.88532	9.3381	9.4897±0.038
3	6.987	6.94782	7.00878	7.02605	7.08399	7.11062	6.7239	6.63459±0.028
4	5.06722	5.03122	5.10356	5.10919	5.15217	5.12873	4.8751	4.81982±0.021
5	3.88986	3.8599	3.91949	3.92179	3.95512	3.92909	3.5688	3.50153±0.016
6	2.77586	2.75385	2.79869	2.79965	2.82341	2.80152	2.6666	2.56139±0.012
7	2.22765	2.20974	2.24576	2.24625	2.26529	2.24747	2.3708	2.20918±0.010

Table 3: A Show difference between theoretical Compton profiles and the measurement. Experimental errors are also shown at few points. The theoretical profiles corresponding to (LCAO-HF)and most favored ionic configuration are presented. The profiles are normalized so that the integral from 0 to 7.0 a.u. is 60.30 electrons. All theoretical values have been convoluted with the residual instrumental function (RIF).

P_z(a.u)	J(P_z) (e/a.u.)		Experimental J(P_z) (e/a.u.)	
	HF	$Gd_2^{+5}O_3^{-5}$	Before DS	After DS
0	28.2558	27.0720	26.089	26.78819±0.082
0.1	27.95897	26.5730	26.055	26.74806
0.2	27.54049	25.9239	26.029	26.50109
0.3	26.9335	25.1122	25.700	25.99456
0.4	26.1193	24.1763	24.736	25.26179
0.5	25.11384	23.1629	23.956	24.42134
0.6	23.94498	22.0769	23.161	23.44132
0.7	22.64312	20.9113	21.801	22.36271
0.8	21.24145	19.6855	20.992	21.24826
1	18.30199	17.2529	18.404	18.69124±0.06
1.2	15.50583	15.0820	15.695	16.01734
1.4	13.19481	13.2600	13.391	13.72486
1.6	11.49125	11.8084	11.980	11.98504
1.8	10.29037	10.6519	10.426	10.59285
2	9.40614	9.67893	9.3381	9.4897±0.038
3	6.59164	7.08399	6.7239	6.63459±0.028
4	4.72422	5.15217	4.8751	4.81982±0.021
5	3.47313	3.95512	3.5688	3.50153±0.016
6	2.6848	2.82341	2.6666	2.56139±0.012
7	2.21625	2.26529	2.3708	2.20918±0.010

References:

[1] N. Singh, S. M .Saini, T. Nautiyal, S. Auluck. Electronic structure and optical properties of rare earth sesquioxides (R_2O_3, R = La, Pr and Nd). J. Appl. Phys, **100**: 083525 **(2006).**

[2] M. Yoshimura and X. Z. Rong, J. Mater. Sci. Letts., **16 (1997)**.

[3] F. X. Zhang, M. Lang, J. W. Wang, U. Becker and R. C. Ewing, Phys. Rev. B, **78:** 064114 **(2008).**

[4]A. M. Pires, M. R. Davolos, C. O. Paiva-Santos, E. B. Stucchi and J. Flor, J. Solid State Chem., **171:** 420 **(2003)** .

[5] G. A. M. Hussein, J. Phys. Chem., **98:** 9657 **(1994).**

[6] N. Hirosaki, S. Ogata and C. Kocer, J. Alloys. Comp., **351:**31 **(2003)**.

[7] L. Petit, A. Svane, Z. Szotek and W. M. Temmerman, Phys. Rev. B, **72 (2005).**

[8] Z. Kaliman, K. Pisk and R.H. Pratt, Phys. Rev. A, **83 (2011) .**

[9] M. J. Cooper, Rep. Prog. Phys. 48, 415 **(1985)** and references therein. Also M. J. Cooper, P. E. Mijnarends, N. Shiotani, N. Sakai and A. Bansil, X-ray Compton Scattering (Oxford University Press, New York, **(2004)**.

[10]. B.L. Ahuja, M. Sharma and S. Mathur, Nucl. Instrum. Meth. B, **244 ,419 (2006).**

[11] D.N. Timms, Compton Scattering Studies of Spin and Momentum Densities, Ph. D. Thesis, University of Warwick, UK, (unpublished) **1989.**
[12] J. Felsteiner, P. Pattison and M.J. Cooper, Phil. Mag., **30 537(1974).**
[13] F. Biggs, L.B. Mandelsohn and J.B. Mann., Atomic Data Nucl. Data Tables, **16 . 201(1975).**
[14] R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M .Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, D'Arco Ph, M. Llunell, CRYSTAL09 User's Manual,University of Torino, Torino**,(2009).**
[15] R. Dovesi, R. Orlando, B. Civalleri, C. Roetti, V. R. Saunders and C. M. Zicovich-Wilson,Z. Kristallogr., **220 (2005) .**

دراسة التركيب الكتروني(Gd_2O_3) بأستخدام تقنية كومبتن

فريد مجيد محمد[1] ، عبدالهادي مردان غالب[2] ، جاكريتي سارهيا[3] ، بامو جاندريا[3] ، اهوجا[3]

[1]قسم الفيزياء ، كلية العلوم ، جامعة تكريت ، تكريت ، العراق

[2]قسم الفيزياء ، كلية العلوم ، جامعة كركوك ، كركوك ، العراق

[3]قسم الفيزياء ، كلية العلوم ، جامعة سوكديا ، الهند

الملخص

في هذا البحث تمت حساب منحني كومبتن ل (Gd_2O_3) بلستعمال طاقة كاما (662.65KeV) المنبعثة من مصدر المشع (20Ci)، وان مطيافية كومبتن ذات متوسط تحليل (0.34 a.u.).البيانات التجريبية لشكل منحني كومبتن قورنت مع الطريقة النظرية المعروفة بالاتحاد الخطي للاوربتالات الذرية وباستخدام برنامج (Crystal 09) .وايضا قورنت مع النموذج الايوني ،ولاحظنا طريقة هاتري فوك ضمن النموذج الاتحاد الخطي للاوربتالات الذرية يعطي افضل التوافق مع النتائج االعملية .وبالنسبة حسابات النموذج الايوني تم افترض عدد من الترتيبات اللكترونية ل($Gd_2^{+X}O_3^{-X}$) حيث ان ($0.0 \leq x \leq 6$) النموذج اقترحت انتقال خمسة الالكترونات من القشرتين (3dو4s)ل Gdالى القشرة (2p) في الاوكسجين .

الكلمات الدالة: استطارة الاشعة السينية،حسابات التركيب الحزمي،نظرية كثافة الدالة،النموذج الايوني.