IBN AL- HAITHAM J. FOR PURE & APPL. SCI. VOL.19 (4) 2006

Charge Transfer Between d-p States in TiO_2 By Employing Compton Scattering Techniques

F. M.Mohammad
Department of Physics,College of Education,University of Tikreet,

Abstract

The compton profiles for TiO_2 have been measured using a 5Ci Am-241 compton spectrometer .A pellet of the oxide was prepared from a polycrystalline powder having a thickness of 1.54 mm ,about 100000 counts have been accumulated at the compton peak .Theoretical compton profiles have been calculated for different ionic arrangements using free atom compton profile for the core electrons.The theoretical and experimental results ahree well for $(Ti)^{+4}(O^{-2})^2$ arrangement which support complete transfer of valence electrons from metal to oxygen ions, i.e., full ionic bonding in this oxide in agreement with available photoemission and other studies .

Introduction

Oxides are an important class of materials because they exhibit several interesting physical properties .It has also been established that their characteristic behavior is related to their electronic structure which remains less well understood .In the last few years progress has been made largely because of the availability of experimental results from xps , UV photoemission and related techniques (1).Regarding the interpretation of these data , mostly mol cular orbital approach has been tried as band structure calculations are not available for most cases due to complicated crystal structure . In recent years, compton scattering technique has been applied successfully to probe the behavior of outer valence electrons in solids , see for example(2,3) . Afew studies have been made on metal oxides . Of these alkaline earth oxides, BeO and MgO , have been studied extensively both theortically as well as experimentally (4,5,6,7,8). Among transition metal oxides (TMO), compton profile of MnO was studied by (9)

where the experimental data was compared with free atom and ionic model. The electron state in TiO was studied by comparing the experimental profiles with that calculated from isolated ions and also with the scattering factor values obtained with the critical voltage effect (10).A compton profile measurement on a single crystal of NiO was made and compared with a simple calculation by (11).Compton profile of magnetite(Fe3O4)was measured across verwey transition by (12).(13) concluded that the 2D-ACAR and compton scattering high resolution momentum experiments are useful tools to probe the electronic structure of the high Tc superconducting Oxides,(14)calculated the electronic structures and dynamic second-order polarizabilities of the clusters Cs2B6O10,Li2B6O10 and CsLiB6O10 by using the intermediate neglect of different overlap with singlet excited configuration interaction method and in combination with the sum-over-states method.(15) investigate the electronic structure of the band width-controlled ruthenates Y2Ru2O7,CaRuO3,SrRuO3 and Bi2Ru2O7 by optical conductivity analysis and estimated some physical parameters which shows that the 4d orbitals should be more extended than 3d ones.

Realizing the fact that there was an utter lack of experimental and theoretical work on TMO's,it was thought of interest to embark upon a systematic study for these systems.In this work, the study on transition metal oxide(TMO' s) namely TiO_2 was reported. Preliminary results on Nb_2O_5 and MoO_3 were reported(16),the measurements on MoO_3 support ionic model in agreement with photoemission studies of (1).

Experiment

The sample used in this study was a thin pellet of 1.54mm prepared by pressing polycrystalline powder.The compton profile measurements have been made using the high intensity compton spectrometer described elsewhere (17).A brief summary of the experimental procedure is given here, Gamma rays from a 5Ci annular Am-241 source were scattered by the sample through a mean angle of 157 ($\pm$1.5) and detected by using a planar intrinsic Ge detector(FWHM 415eV at 60KeV).The channel width was about 58.6eV which corresponds to a little less than 0.1 a.u. of momentum.About 100000 counts/channel were accumulated at the compton peak.A separate measurement was made without any sample

to obtain the background contribution which was then subtracted point to point from the measured data after being scaled properly to the measurement time.Then the profile was corrected for, i)instrument resolution ii)sample absorption iii)energy dependence of the differential compton scattering cross-section and iv)multiple scaterring.Finally, the experimental compton profile of TiO_2 was normalised to have area of 17.69 electrons which corresponds to the area of the free atom profile of TiO_2 between 0 to 7 a.u.

Theoretical calculations

The scattering angle is found by the relation :

$$\cos\theta = 1 - mc^2 / EE'(E - E') \text{---------- [1]}$$

Where in this work , E = 59.537 KeV ,E` = 48.627 KeV ,mc2 =511 KeV.

The compton profile J(Pz) for a polycrystalline is related to the averagee

electron momentum density $< \rho(p) >$ as:

$$J(Pz) = 2\pi \int < \rho(p) > p\, dp \text{---------- [2]}$$

Where the integration is over the plane of constant Pz and $< \rho(p) >$ is the spherically averaged electron momentum density .

In order to compare these measurements, it would have been most useful if band structure result was available, since that was not the case,asimple approach was tried depending on ionic arrangements.

Case.1: The compton profiles(CP) for the case when complete transfer of valence electrons to oxygen 2p orbitals was considered.This compton profile for the ionic arrangement $(Ti)^{+4}\ (O^{-2})^2$ was computed in terms of the simple ionic model.Compton profiles for the various orbitals were taken from the tables (18, 19).For obtaining the contribution of O^{-2},two electrons were added to 2p orbitals of oxygen increasing their contribution suitably that is :

$$J(Pz)\{(Ti)^{+4}\ (O^{-2})^2\} = J(Pz)\{1S^2\text{----}3d^0\}\ \text{metal} + \{1S^2\text{-----}2P^6\}\ \text{oxygen-------[3]}$$

Case.2: Partial ionicity : CP calculated for $(Ti)^{+2}(O^{-1})^2$ .Here we started with the experimental compton profile of the metal Ti and found out the contribution for each valance electron by subtracting the corresponding core-contribution and dividing by the number of valence electrons.This contribution after proper multiplication was

removed from the contribution of metallic constitutions and then the contribution due to O^{-1} was added as discussed above that is :

J(Pz) exp.$\{1S^2$----$3d^4\}$- J(Pz) core$\{1S^2$---$3P^6\}$= J(Pz) valence -------[4].

J(Pz) for one valence electron = J(Pz) valence / 4 ---------- [5]

Case.3: Super position model :The free-atom compton profile was calculated for the sample which was determined directly from the tables of(18,19)by superposing the contributions of constituent atoms.This represents the case of neutral oxygen atom.All the theoretical values have been convoluted with the residual instrumental function (RIF) of the spectrometer for a proper comparison with the experiment, because no deconvolution procedure can remove the instrumental broadining completely due to statistical noise ever present in the experiment (20).The various theoretical values are normalised as above.

Results and Discussion

The final compton profiles obtained as per the procedure described in sec . II and III are given in table 1. The experimental values are given in column 5. The various theoretical values are given in columns (2- 4).Fig.1shows the different profiles given in table (1)

Comparing first the various values in the high momentum region(i.e.,>4a.u.), it is seen that all theoretical values are nearly equal.

This is so because in this region the contribution of valance electrons is insignificant and only core electrons contribute. Their values are the same in all models and have been obtained from free atom values. Interestingly, these theoretical values are already very close to the experiment. This once again confirms the fact that the inner electrons remain almost unaffected in the bond formation and the simple atomic model provides a reasonable description for these electrons.

In order to investigate the behaviour of valence electrons we compare the various values in the low momentum region. It is seen that the free atom values(column 2) differ appreciably than the ionic model. In fig.2 , we plot the difference ΔJ(theory-experiment) for the various ionic model values given in table2. It is seen that up to 1.2a.u. the experimental values are larger than the theoretical values of col.3 while beyond 1.2 its getting reversed, the theoretical values of col.4are greater than the experimental values up to 0.3a.u., while it is

getting reversed beyond 0.3a.u. upto 1.6a.u., its getting reversed again, that's the theoretical values become larger than the exp. values. After 1.8a.u. differences are very small ,i.e., the theoretical and experimental values agree very well.To determine the best configuration we have calculated the total square deviation ,i.e., Δ^2 given as:

$$\sum_{Pz=0}^{7a.u.} | \Delta J(\text{Theo.} - \text{Exp.}) |^2 \qquad \text{----------[6]}$$

The values being 0.89175 for $\sum_{Pz=0}^{7a.u.} | \Delta J\{(Ti)^{+4}(O^{-2})^2 - \text{Exp.}\} |^2$,

3.4498 for $\sum_{Pz=0}^{7a.u.} | \Delta J\{(Ti)^{+2}(O^{-1})^2 - \text{Exp.}\} |^2$

12.308 for $\sum_{Pz=0}^{7a.u.} | \Delta J\{\text{free} - \text{Exp.}\} |^2$.

IT turened out that Δ^2 was lowest for $(Ti)^{+4}(O^{-2})^2$.

Conclutions

In this work, the study of compton profile of TiO_2 was reported . It is seen that these measurements clearly favour the d(0) type distribution ,i.e., complete transfer of valence electrons to oxygen atoms. These results are in excellent agreement with the earlier conclusions based on x-ray fiourescence (XPS) and other studies on MoO3 and V_2O_5. However, more experimental and theoretical works are needed.

References

1-Werfel,F. and Minni,E. (1983) J.Phys.C;Solid State Phys.,16:6091.

2-Sharma,B.K.;Ahuja,B.L.;Singh,H. and Mohammad,F.M. (1993) compton profile of molybdenum Pramana Journal of Physics India 40(5)

3-Mohammad,F.M.;Sharma,B.K.;Singh,H. and Ahuja,B.L. (1989) study of electron distribution in Rh by compton scattering technique"Phys.Stat.Solidi,B152:145

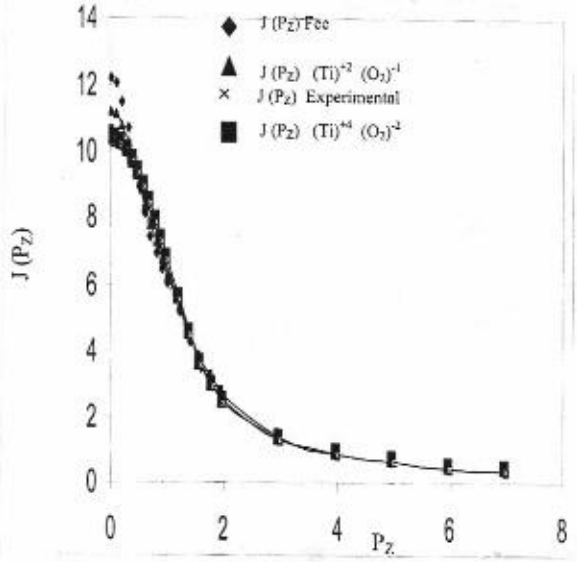
4-Fukamachi,T.and Hosoya,S. (1970) electron state in BeO studied by compton scattering measurement"J.Phys.Soc.Japan ,28: 161.
5-Fucamachi,T. and Hosoya,S. (1971) electron state of an O2 atom in MgO. J.Phys.Soc.Japan, , 31:980
6-Togawa,S.;Inbeinen,O. and Manninen,S."The compton profile of MgO"J.Phys.Soc.Japan,30: 1132(1971).
7-Aikala,O.;Paakkari,T. and Manninen,S. (1982) Acta Cryst.,A38:155
8-Podloucky,R.andRedinger,J. J.Phys.C.Sol.Stat.Phys.16:6955(1984)
9-Weiss,R. (1972)J. The compton profile of scandium Phil.Mag.,26: 761
10-Terasaki,O;Watanbe,D;Fukamachi,T;Hosoya,S.andShimazu,M. (1972) electron state in TiO studied by measurements of compton profile scattering factors Phys.Lett,40(A): 357
11-Fukamachi,T.;Hosoya,S;Iway,K.and Hyakawa, K. (1973) Anisotropy of compton profile found in nickel oxide single crystal"Phys.Lett.,42A:477.
12-L asser,R.;Singru.R.M. andLengeler,B.(1978)Sol.Stat. Comm.,25:345.
13-Barbielini,B.and Platzman,P. (1997). Momentum density of high Tc copper oxide`s.arxiv:cond-mat/9710216, 21
14-Cheng,W.D.;Chen,J.T.;Lin,Q.S.;Zhang,Q.E.and Lu,J.X. (1999). cluster modeling of electronic structure and nonlinear properties for the optical materials MB6010.Phys.Rev.B. 60(16)
15-Lee,J.S.;Lee,Y.S.and Noh,T.W. (2001) optical investigation of the electronic structure of Y2Ru207,CaRuO3andBi2Ru207 Phys.Rev.B. 64:245107
16-ohammad,F.M.;Sharma,B.K.;Ahuja,B.L.andUshaMittal (1987) Investigation of electronic structure of some oxides by compton ScatteringtechniqueProc.Solid Stat.Phys.Symo., B.A.R.C, Bombay,India
17-Mohammad,F.M . (1994) Compton profile of Tungsten. J.Ed.Sc.,17,Mosul,Iraq
18-Weiss,R.J;Harvey,A.and Philips,W.C. (1968)Compton line shapes for Hartree-Fock wave functions .Phil.Mag.,17:241.
19-Biggs,F.;Mendelsohn,L.B.and Mann,J.B. (1975) Hartree-Fock compton profiles for the elements Atomic Data and Nuclear Data Tables,16:201
20-Paatero, P.,Manninen,S.and Paakkari, T. (1974) Deconvolution in compton profile measurements Phil.Mag.,30:1281

Table(1) Theoretical and experimental compton profiles of thin 1.54mm titanium dioxide (TiO_2) All theoretical values have been convoluted with the residual instrumental function (RIF). These values have been normalised to 17.69 electrons as discussed in the text .

Pz	Theo.free atom(CP) J(Pz) {case.3}	Theo.(CP) $(Ti)^{+4}$ $(O^2)^{-2}$ {case.1}	Theo.(CP) $(Ti)^{+2}$ $(O^2)^{-1}$ {case.2}	Experimental (CP) J(Pz) exp.
0	12.232	10.17	11.252	10.429
0.1	12.06	10.147	11.172	10.381
0.2	11.511	10.001	10.802	10.248
0.3	10.748	9.801	10.325	10.032
0.4	9.836	9.487	9.694	9.739
0.5	8.952	9.12	9.063	9.372
0.6	8.140	8.662	8.421	8.943
0.7	7.479	8.164	7.833	8.453
0.8	6.932	7.618	7.289	7.912
0.9	6.482	7.06	6.777	7.337
1.0	6.057	6.498	6.288	6.743
1.2	5.192	5.432	5.321	5.559
1.4	4.294	4.501	4.404	4.481
1.6	3.502	3.726	3.621	3.583
1.8	2.912	3.105	2.984	2.892
2.0	2.488	2.62	2.515	2.391
3.0	1.312	1.344	1.306	1.264
4.0	0.88	0.878	0.87	0.837
5.0	0.609	0.631	0.631	0.611
6.0	0.447	0.446	0.447	0.444
7.0	0.329	0.33	0.33	0.321

Table(2) The differences between theory a nd experiment results for TiO_2

J(Pz) {Theo.-Exp.}			
Pz	$(Ti)^{+4}(O^{2})^{-2}$ _ Exp.	$(Ti)^{+2}(O^{-2})^{1}$ _Exp,	$(Ti)^{+0}(O^{2})^{-0}$ _Exp.
0	-0.2590704	0.8229294	1.8029
0.1	-0.2337093	0.7912903	1.6792
0.2	-0.2467299	0.5542698	1.2632
0.3	-0.2311401	0.29286	0.7158
0.4	-0.2519693	-0.044969	0.09703
0.5	-0.2522602	-0.3092604	-0.42026
0.6	-0.2811003	-0.5221005	-0.80309
0.7	-0.2885008	-0.6195002	-0.9735
0.8	-0.2935	-0.6225	-0.9794
0.9	-0.2772002	-0.5602002	-0.8552
1.0	-0.2448001	-0.4548002	-0.6858
1.2	-0.1271	-0.2381001	-0.3671
1.4	0.01989	-0.0771	-0.18709
1.6	0.1435001	0.0385	-0,08049
1.8	0.2126	0.09159	0.01959
2.0	0.2292998	0.1243	0,09729
3.0	0.0797	0.0417	0.0477
4.0	0.0408	0.0328	0.0428
5.0	0.0205	0.0205	-0.001499
6.0	0.0017	0.0027	0.0027
7.0	0.0086	0.0086	0.0076



Fig(1)Comparison of theoretical and experimental compton profiles for polycrystalline TiO_2 All theoretical values have been convoluted with the RIF

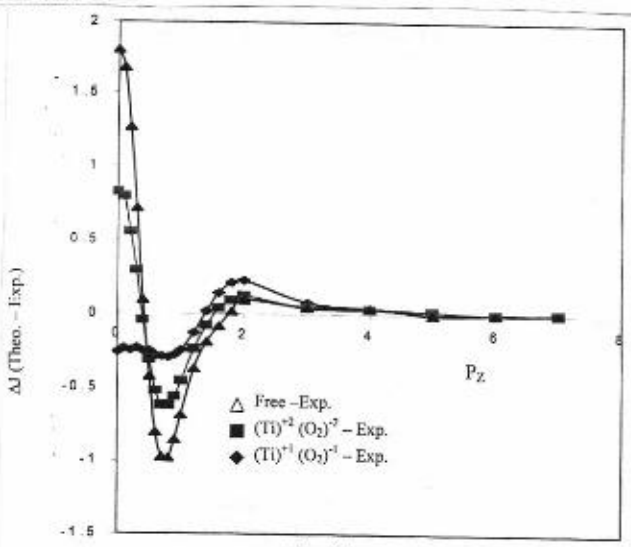


Fig (2)

Fig.(2) The differences between theoretical and experimental compton profiles of TiO_2

مجلة ابن الهيثم للعلوم الصرفة والتطبيقية المجلد 19 (4) 2006

انتقال الشحنة بين المدارين d-p في ثاني أو كسيد التيتانيوم (TiO_2) باستخدام تقنية استطارة كومبتون

فريد مجيد محمد
قسم الفيزياء ،كلية التربية ، جامعة تكريت

الخلاصة

لقد تم قياس شكل منحنى كومبتون لثاني أوكسيد التيتانيوم TiO_2 باستخدام المصدر المشع الامريشيوم (Am- 241، 5 Ci)و حضرت العينه من بودرة متعددة البلورة للاوكساید وبسمك 1.54 mm وتم الحصول على 100000 عد في ذروة كومبتون . شكل منحنى كومبتون تم حسابه نظريا لمختلف الترتيبات الايونية باستخدام قيم منحنى كومبتون للذرة الحرة لإلكترونات اللب . احسن توافق بين القيم النظرية المحسوبة والعملية المقاسة كان للترتيب $Ti^{+4}(O^{-2})^2$ والذي يساند الانتقال الكلي لإلكترونات التكافؤ من المعدن إلى الأوكسجين متوافقا مع الدراسات الخاصة بالانبعاث الضوئي ودراسات أخرى .