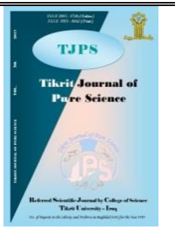
Tikrit Journal of Pure Science 23 (3) 2018

ISSN: 1813 – 1662 (Print)
E-ISSN: 2415 – 1726 (On Line)

TJPS

TIKRIT JOURNAL OF PURE SCIENCE

Journal Homepage: http://main.tu-jo.com/ojs/index.php/TJPS/index



Electronic configuration of vanadium carbide (VC)

Fareed M. Mohammed , Sameh H. Salih , Abdulkader A. Hassan , Shalash A. Mohammed
Department of physics , College of Science , University of Tikrit , Tikrit , Iraq

ARTICLE INFO.

Article history:
-Received: 29 / 5 / 2017
-Accepted: 5 / 12 / 2017
-Available online: / / 2018

Keywords: Electron momentum density, Impulse Approximation, Compton Scattering.

Corresponding Author:

Name: Shalash. A. Mohammed

E-mail: Samheph@yahoo.com
Tel:
Affiliation:

Abstract

In this paper we used renormalized free atom model to study the electronic configuration of vanadium carbide compound. The theoretical values were obtained after finding the values of each element separately and using the superposition model to find the best electronic arrangement. These results were compared with experimental values measured by using high energy (661.65 keV)ɣ-radiations from a ^{137}Cs source. We observed two things, first; if half the density of the electronic momentum of the compound is concentrated in vanadium we get the electronic order (2s^{1}-2p$^{1.5}$)C+(3d$^{+5.5}$-4s^{1})V. second, if full the density of the electronic momentum of the compound is concentrated in vanadium we got the electron order (2s^{1}-2p^{0})C+(3d^{+7}-4s^{1})V .The best results out of these were when the full electron transfer from carbon to vanadium occurs.

1-Introduction

Vanadium carbide is the inorganic composite with the mode VC.It is an immensely hard refractory ceramic material[1]. It is probably the stiffer metal-carbide known[2] and is of attentions because it is predominant in vanadium metal and alloys[3]. Vanadium carbide be isomorphous with vanadium monoxide, it crystallizes in the freestone demandingly structure. because' VC and VO are miscible, demos of VC typically contours an faunlts of the oxide[4].It is outputted by heating vanadium oxides with carbon at around 1000°C. Vanadium carbide can be ingredient in the (111) orientation. For all that VC is thermodynamically settled, it shuns to V_2C at higher temperatures. Vanadium carbide is used as an additive to tungsten carbide to glossiness the carbide crystals to improve the speciality of the Cermet. Vanadium carbide has modulus coefficient of virtualy 380 Gpa[4].

2.Compton Scattering

Inelastic scattering (Compton scattering) is a forceful and impressionable probe for investigating electronic structure of varity of materials. The Compton redounding was discovervd by Sir A.H. Compton in 1923[5,6]. For this cranky discovery, Compton was honoerd by noble award in (1927). At that time, Compton's effect was very consequential to the scientific community because it exemplified that γ-rays can not act only as waves but also as particles ,i.e. photons. In comparison to other rival technique, Compton scattering has several advantages. In 2-dimensional angular correlation of annihilation radiation (2D-ACAR) sample should be kept at low temperature and pure samples are needed but the Compton scattering does not require low temperature and is insensitive to microscopic defects. The limitation of this technique is the low resolution dictated by the detector but that has been overcome with the application of synchrotron radiation sources, together with sophisticated crystal optics further, there is no modification by the probe in system. Essentially in Compton scattering one can measure the Compton line shape,(the intensity distribution of energy broadened Compton scattering radiation) known as Compton profile which is the projection of electron momentum density along scattering vector direction. Thus ,such a study yields the ground state momentum distribution of electron in the sample[7].

3.Basic Theory of Compton scattering

The basic and important condition in Compton scattering is that, The electron should be free and fixed, in another meaning, connecting the electron with the nucleus is minimal. Also rely on the impulse approximation (IA) theory in the account which states, {Photon interaction with Electron be instantaneous without changing the properties of the electron}. In Compton scattering, the high-energy photon interacts with the electron in the outer orbit of the atom in most cases leading to the transmission of part of photon energy to the electron. The Photon with new energy will be dispersed in a new direction different from the incidence direction at an angle (Φ). The overall momentum in this process most be conserved. It can happen more than scattering if the photon have high energy. The process will change the wavelength, this change in wavelength is called Compton shift[5],and is given by

$\Delta\lambda=\lambda_2-\lambda_1= (h/m_oc)(1-\cos\phi)$. (1)

Where λ_1 and λ_2 are the wavelengths of incident and scattered photons and m_o is the mass of the target electron.

This equation depends only on the angle of dispersion and does not depend on the nature of dispersion and wavelength. This can be written in the form of energy as

$$w_2=\frac{w1}{1+\frac{w1}{m_\circ c^2}(1-cos\phi)} \qquad (2)$$

where w_1 and w_2 are the energy of photon before and after scattering respectively.

The above equation proves to us that the electron mostly be free and at rest in the target. The important, Compton observed the position of Compton peak experimentally exactly as predicted by equation(1) but the line width was much larger than that could arise due to difference of angles dispersion, accuracy of detector etc. The sum of these effects has been corrected by Du Mond, Kirkpatrik, Ross, Jauncy and several other workers to explain this broadening in Compton line shape. According to Du Mond and Kirkpatrik [8], Ross is stood with the theory that the movement of electrons in the materials may have caused a cause of expansion in Compton line shape. This idea was transferred into a formal theory by Jauncy[9]. The movement of these electrons causes excitation in Compton line described with doppler broadening by Du Mond [10]. In the end, the movement of the electron was organized into a basic theory, the Compton shift, Eq(1) changes to

$$\lambda_2-\lambda_1=(2h/m_oC^2)x \ \sin^2(\frac{\phi}{2)})+2(\lambda_1\lambda_2)^{1/2}(\frac{Pz}{mc})\sin(\frac{\phi}{2}) \qquad (3)$$

where p_z is the electronic linear momentum along the direction of scattering.

As in the Doppler line definition Compton profile calculated by electronic momentum on the coordinate z –component of the electronic in the scatter i.e.

$$J(pz) = \iint \ x^*(\vec{p})x(\vec{p})\, dp_x\, dp_y \qquad (4)$$

Where $x(\vec{p})$ is the electron wave function in the momentum space.

4. Renormalized free atom model and Compton profile

The Renormalized free atom (R.F.A) model[11], which has been successful in computation of Compton profile of heavy transition metals and lanthanides Renormalized free atom model, the atomic wave function is specific at the Wigner-Sitez radius and renormalized to one per electron within the Wigner-Sitez radius sphere to derive the approximate crystal wave function. The (RFA) way was used first by chodorow[12].This way considers the atom as not free, but confined to apointed cell in the solid. The calculation starts from Hartree-fock wave function which is specific at WS(R_o) and Renormalized to unity within this sphere to preserve the charge neutrality.The new wave function $R_{nl}(r)$ is given by[13].

$$R_{nl}(r)=\begin{cases} N_{nl}\, R_{nl}^{atomic(r)} & r\le R_o \\ 0 & r\ >\ R_o \end{cases} \qquad (5)$$

where $R_{nl}^{atomic(r)}$ the atomic radial wave founction for the state within quantum numbers n,l and N_{nl} is definedby.

$$N_{nl}=\int_0^{Ro} |\, R_{nl}^{atomic(r)}\ |^2 r^2 dr \qquad (6)$$

The fresh wave function is then utilized in most computations.In this approach the solid is formed from individual atoms approximated in same form which they actually enter the solid before being bound together .In conection with the success of this simple model, as well as Compton works [13,14] have shown that the model gives quantitatively concordant compliments of consequential band structure peculiiarities and also an construing of cohesion in the commute series. Even in intricate band theory caluclation, renormalized free atom model is invoked to obtain the one electron potential [15]. Berggren [16] has studid the aggregative behavior of the renormalized free. founction(4s electron in V) and has subordinate it to be a bona representation of the true crystal wave function at K=0. It is anticipated that the effects of renormalization are eldest for the outermost ``s`` electron because unlikly 25-30% charge is content in the Weigher-Sitez(WS)sphere.For ``d`` electron we will now proceed to the appraisal of the ferrying Compton profile for the 4s band ,for this intend we have to take into consideration the momentum metamorphosis of Bloch function,which for cubic structures is given by[17].

$$\Psi_k(p)= N\delta(P-K1K_n)\Psi_k^c(p) \qquad (7)$$

Where k_n is the reciprocal lattice vector ,and N is the overall number of atoms, and the $\Psi_p^c(p)$ is defined as

$$\Psi_p^c(p)=(2\pi)^{-3/2} \int e^{-ip.r}\, \Psi_k(r)\, dr \qquad (8)$$

The zone integration is over the (WS) polyhedron,in the idiomatic cell apprpximation:

$$\Psi_k(r)= e^{i.k.r}\Psi_k \qquad (9)$$

The transfrom in equation (5) trivializes to

$$\Psi_k^c(p)=\Psi_0^c(k_n) \qquad (10)$$

K_n=p-k. some carefulness must be existent in prizing $\Psi_k(p)$. The region of integration got at once be replaced by the (WS) sphere. To preserveable normalization of $\Psi_k(p)$ in eq(7) we write.

$$\Psi_k^c(p)=2\pi^{-3/2}\int \ e^{-ik.r}[\Psi o(r) - \qquad (11)$$
$$\Psi o(Ro)]dr + (2\pi^{-3/2}\Omega o\delta(kn,0))\Psi o(Ro)$$

The spherical approximation may now be performed for this integral[18]. The momentum density per atom is given.

$$N(p)=2\sum_k \delta\,(p-k,k_n)|\Psi_0^c(kn)|^2 \qquad (12)$$

Where the k runs over all occupied states and the factor 2 comes from summation over spin. If we suppose spherical population of s-states then the spherical interceded of n(p) is readily taken on. The Kronecker(δ)in equation (12) exchange by the prerequisite K_n-P $\leq P_F$ and we obtain[19].

$< n(p) > = 2\sum_{n=0}^{\infty} Fn(p)\,|\Psi_0^c(kn)|^2$ (13)

For n≠0

$F_n(p)=N_n[P_F^2-(k_n-p)^2]\,/4k_np$

If p ϵ ($k_n - P_f$, $k_n + P_f$) and is zero otherwise, N_n is the number of reciprocal lattice pointes in the n shell and P_F is the fermi momentum for the S- electron.

For n=0

$F_0(p)=\begin{cases}1 & p\leq PF\\ 0 & P>PF\end{cases}$ (14)

Elemental integration eventually gives the ferrying for isotropic compton profiles as[19].

$J_{4s}(q)=4\pi\sum_{n=0}^{\infty}|\Psi_o^c(kn)|^2\,Gn(q)$ (15)

For n≠0

$$Gn(q)=\begin{cases}0 & q>kn+pf\\ \bar{G}n(q) & q\in(kn-pf,kn+pf)\\ \bar{G}n(kn-pf) & q<(kn-pf)\end{cases} \qquad (16)$$

Where the function $\bar{G}(x)$ is defined as.

$\bar{G}n(x)=Nn\{(P_F^2 - K_n^2)(k_n + P_F-X) - \frac{1}{3}[(K_n+P_F)^3 - X^3]+K_n[(K_n+P_F) - X^2)\}/4Kn$ (17)

For n=0

$G_0(q) =\frac{1}{2}(P_F^2 - q^2)$ (18)

If q > PF and zero other wise.

The above model which does not include, as mentioned before hybridization of d bands, is not useful for data on crystalline samples. It does ,however, give an opportunity to vary the distribution of band electrons in s-d state to know the most electron configuration for a given metal. the Compton profile is obtained by superposing the contribution of core electrons and the band electron, using the above formula ,the computer programs were written and tested previously [20].

5- Results and Discussion

In this work we utilize (RFA) model to study the Compton profiles of Vanadium Carbid (VC). Wherein we used the superposition model in the calculation to study Compton profile through emploxing the values which find out for each Carbon and Vanadium. These results were approximate with the experimental values [21]. This work divides into two steps, firstly if half electrons are transferred from the wrapper(P) in Carbon To the wrapper (d) in Vanadium we got the formula($2S^1+2P^{1.5}$)C—($3d^{+5.5}$-$4S^1$)V as shown in table I.And if the full electron transfer from the wrapper (P) in Carbon to the wrapper (d) in Vanadium we gott the formula ($2S^1+2P^0$)C—($3d^7+4S^1$)V as shown in table II . If we compare the results we obtained from the(RFA) model and the results extracted by using different density functional schemes, namely local density and generalized gradient approximations (LDA and GGA, respectively) and the hybri dization of DFT and HF (B3LYP) [21],as shown in table (I), we find that the values extracted by RFA are closer to the values of the experiment [21]. This enhances the efficiency of the(RFA) model. If we employ these values to represent them, we observe the difference between the density of electrons involved in the interaction as in table (II), we find that in the case of the transfer of all electrons from carbon to vanadium, electronic density is close with the electronic density of the experiment [21]. So the most efficient electronic arrangement is ($2s^1+2p^0$)C_($3d^{+7}+4s^1$)V. To find the difference between theoretical and practical values we used the following equation[19].

$\sum J(P_Z)=[\sum J(P_Z)_{theore}-\sum J(P_Z)_{expt}]$ (19)

After that, we represent these values as shown in Fig(2). We will use this table to draw Compton line carve as shown in Figs. {1,2}, which show the difference between Compton's theoretical and practical curves. where we observe the convergence of Compton's theoretical and practical curves within the momentum zone between (0-1.5a.u.) which belongs to the external packaging. The zone between (3-7 a.u.) shows a perfect match because of the internal electrons involved in the reaction. and the shape of difference between our theoretical and the experimental results is shown in Figs{3,4},Which show Compton's curves for the difference between practical and theoretical values Where we found that the least difference between practical and theoretical values is(1.094167) curved compton. Note that if all the electrons are transferred from carbon to vanadium, the area under the curve is approximated with the area under curve of the experiment, Which represent the number of electrons involved in the interaction.

Table I: Theoretical results of Compton profile of Vanadium carbide (VC) compared with experimental value[21], and with the theoretical values that were found by(LCGO)[21]. Half the density of the electronic momentum of the compound is concentrated in the orbital (d) All the quantities are in atomic units

Pz a.u.	Free atom	Free electron	RFA Vanadium	Carbon	VC Superposition Present work	LCGO [20]	EXPT [20]
			Core+($3d^{5.5}$-$4s^1$)	$2s^1$+$2p^{1.5}$			
0	10.27	7.549207311	5.52020	1.842	7.3622	8.231	7.048
0.1	9.86	7.52471531	5.5026	1.821	7.3236	8.034	7.042
0.2	8.87	7.402276736	5.4220	1.759	7.181	7.875	6.942
0.3	7.75	7.167001616	5.2795	1.657	6.9365	7.647	6.79
0.4	6.82	6.895367125	5.1222	1.522	6.6442	7.326	6.63
0.5	6.13	6.541784728	4.9278	1.367	6.2948	6.909	6.406
0.6	5.6	5.977741283	4.5954	1.207	5.8024	6.427	6.153
0.7	5.18	5.406562005	4.29144	1.051	5.34244	5.926	5.889
0.8	4.8	4.96539816	4.14639	0.91	5.05639	5.435	5.541
1	4.141	4.18323248	3.7999	0.6822	4.4821	4.515	4.857
1.2	3.561	3.65795192	3.394111	0.5237	3.917811	3.732	4.096
1.4	3.05	3.17170048	2.976656	0.417	3.393656	3.109	3.396
1.6	2.614	2.74023556	2.5727	0.349	2.9217	2.613	2.851
1.8	2.241	2.3602804	2.2070	0.29803	2.50503	2.224	2.405
2	1.936	2.04480384	1.8943	0.2630	2.1573	1.878	2.06
3	1.067	1.12613168	0.9999	0.1551	1.155	1.024	1.131
4	0.7186	0.756732808	0.6569	0.092	0.7489	0.712	0.721
5	0.5219	0.548748492	0.47888	0.054	0.53288	0.523	0.513
6	0.3862	0.405924244	0.35815	0.0319	0.39005	0.375	0.373
7	0.2866	0.300677484	0.26928	0.0189	0.28818	0.278	0.277

Table II: Theoretical results Compton of profile of Vanadium carbide (VC) compared withexperimental value[21]. and with the theoretical values that were found by (LCGO)[21]. Full the density of the eletronic momentum of the compound is concentrated in the orbital (d), All the are quantities in atomic units

P_Z a.u.	Free atom	Free electron	RFA Vanadium	Carbon	VC Superposition Present work	LCGO [20]	EXP [20]
			Core+($3d^7$-$4s^1$)	$2s^1$+$2p^0$			
0.0	10.27	7.549207311	5.8952052	1.11	7.057771	8.231	7.048
0.1	9.86	7.52471531	5.8776669	1.089	7.030543	8.034	7.042
0.2	8.87	7.402276736	5.7970909	1.032	6.899091	7.875	6.942
0.3	7.75	7.167001616	5.6545927	0.945	6.66011	7.647	6.79
0.4	6.82	6.895367125	5.4957483	0.843	6.41205	7.326	6.63
0.5	6.13	6.541784728	5.2998272	0.737	6.105533	6.909	6.406
0.6	5.6	5.977741283	4.9629771	0.639	5.57045	6.427	6.153
0.7	5.18	5.406562005	4.65149943	0.552	5.015131	5.926	5.889
0.8	4.8	4.96539816	4.49589943	0.48	4.836723	5.435	5.541
1	4.141	4.18323248	4.12099094	0.3762	4.451199	4.515	4.857
1.2	3.561	3.65795192	3.67941161	0.3137	3.994017	3.732	4.096
1.4	3.05	3.17170048	3.2241563	0.2754	3.51849	3.109	3.396
1.6	2.614	2.74023556	2.78274119	0.253	3.057242	2.613	2.851
1.8	2.241	2.3602804	2.38408968	0.23309	2.634454	2.224	2.405
2	1.936	2.04480384	2.041198074	0.21795	2.270352	1.878	2.06
3	1.067	1.12613168	1.056462783	0.14715	1.204607	1.024	1.131
4	0.7186	0.756732808	0.678710338	0.09085	0.76823	0.712	0.721
5	0.5219	0.548748492	0.487611971	0.05387	0.540375	0.523	0.513
6	0.3862	0.405924244	0.361800022	0.0318	0.392516	0.375	0.373
7	0.2866	0.300677484	0.27089	0.018909	0.28915	0.278	0.277

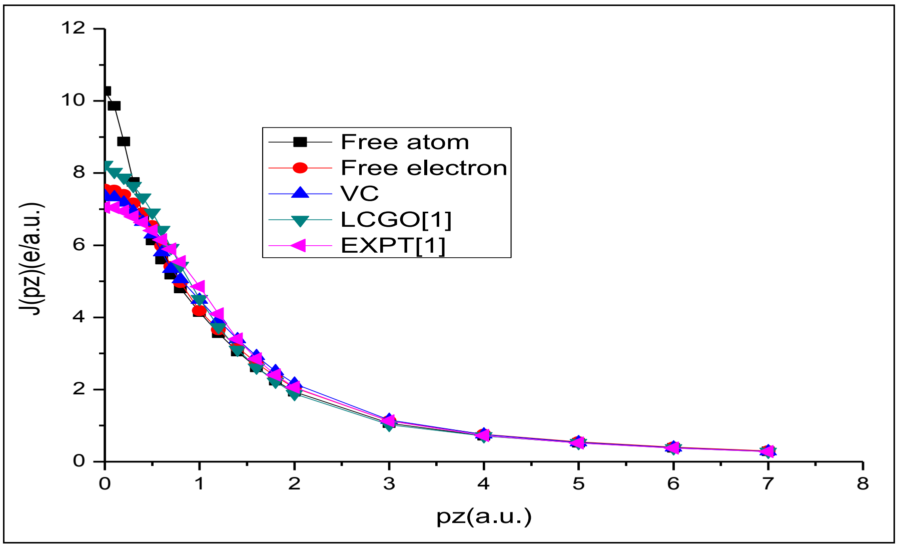


Fig.(1) Comparison of theoretical values with experimental[21] Compton profiles for (VC),when half electron transferred from p_c Carbon to the d_v Vanadium

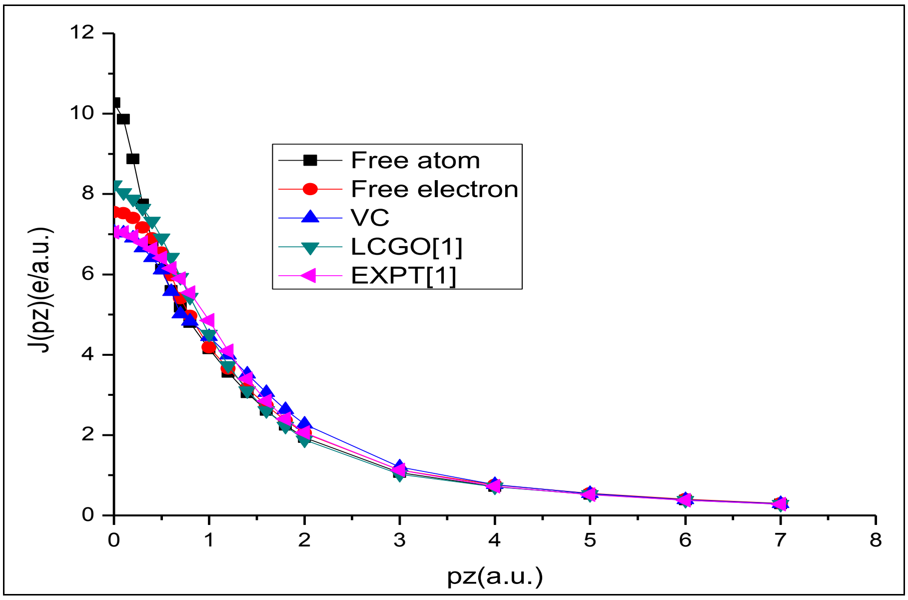


Fig.(2) Comparison of theoretical values with experimental([21] Compton profiles for (VC),when full electrons are transferred from p_c Carbon to the d_v Vanadium .

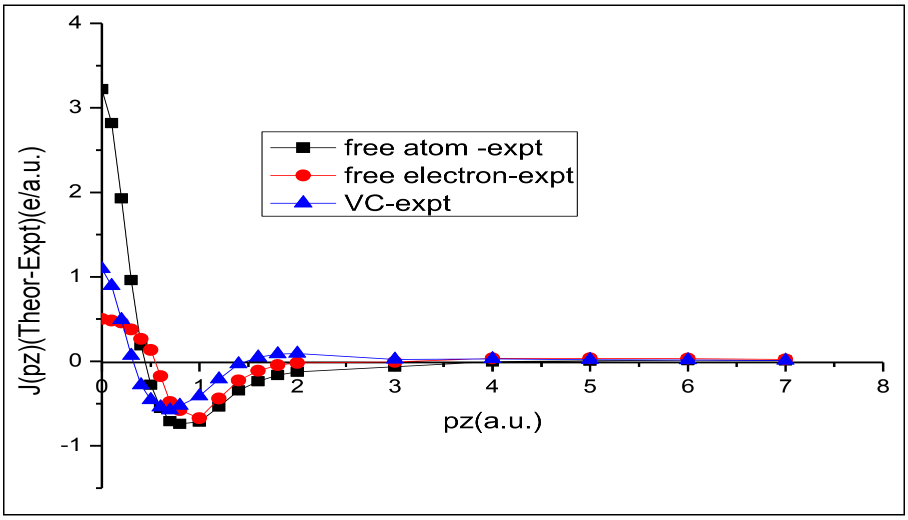


Fig. (3) Difference between our theoretical calculations and experimental results [21] when half electrons are transferred from Carbon to Vanadium

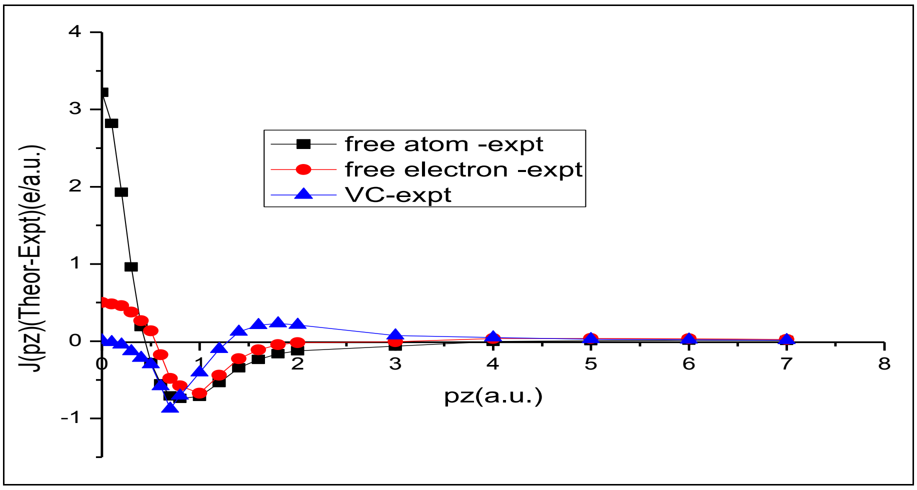


Fig. (4) Differences between our theoretical calculations and experimental results[21] when full electrons are transferred from Carbon to Vanadium.

References

[1]. L ,Lide, D, David R.," Handbook of Chemistry and Physics" (87 ed.), Boca Raton, FL: CRC Press, pp. 4–93 (1998).

[2]. PPM Jump UP. "Ceramic and Cermet Composite Powders - PPM Ltd.". Retrieved 13 September 2016 .

[3]. Günter Bauer, Volker Güther, Hans Hess, Andreas Otto, Oskar Roidl, Heinz Roller, Siegfried Sattelberger "Vanadium and Vanadium Compounds" in Ullmann's Encyclopedia of Industrial Chemistry, 2005, Wiley-VCH.

[4]. R. Hannink, M. Murry, "Elastic moduli measurements of some cubic transition metal carbides and alloyed carbides". Material Science. **9**: 223–22. (1974)

[5]. A.H. Compton, phys. 21, 483 (1923)

[6]. A.H. Compton, phys. 22, 409 (1923).

[7]. J. W. M. Du Mond. Phys. Rev. 33,643(1929).

[8]. J.W. M. Du Moud. And H. A. Kirkpatrik, Phys. Rev. 52, 419(1937).

[9]. G. E. M. Jauncy, phys, Rev. 24,204(1924).

[10]. J. W. M. Dond. Phys. Rev. 33,643(1929).

[11]. K.F. Berggren, phys. Rev. B6 2156-61,(1972).

[12]. M .Chodorow, phys. Rev. 55,675,(1939).

[13]. B. Segall, phys. Rev. 125, 109,(1962).

[14]. L. Hodges, R.E. Watson, H. Ehrenreich, phys. Rev. B5, 3953(1972).

[15]. C.D. Gelatt, H. Ehrenreich, R.E. Watson, phys. Rev. B6,Vol. 15, No.4,1613-28 (1977).

[16]. H. Singh, Ph. D thesis (unpublished) submitted to the university of Rajasthan (1986).

[17]. V.R. Saunders, R. Dovesi, C.roetti, R. Orlando, C.M. Zicovich-Wilson, N. M. Harrison, K. Doll, B. Civalleri, I. J. Bush, Ph. D' Arco and M. Liunell, CRYSTALO3 User Manual, University of Torino, Torino(2003).

[18]. S.Berko, and J.S. Plasket.,"electron oh annihilation radiation in oriented single metal crystals", Phys. Rev. 112,1423.(1990).

[19]. J.P. Perdew, K. Burke, M. Ernzerhof. Phys. Rev. Lett.,77:3865.(1996).

[20]. B. Hammer, L. B. Hansen, J. K. Norskov." Improved adsorptiov energetic within density-functional theory using revised perdew-Burke-Emzerhof functionals". Phys. Rev.B,59: 7413(1999)

[21]. Ritu Joshi, Jagrati Sahariya, B.L. Ahuja (2011)″ Compton scattering study and electronic properties of vanadium carbide‶.

الترتيب الالكتروني لمركب كاربيد الفناديوم (VC)

فريد مجيد محمد ، سامح حميد صالح ، عبد القادر علي حسن ، شلاش عسل محمد
قسم الفيزياء ، كلية العلوم ، جامعة تكريت ، تكريت ، العراق

الملخص

في هذا البحث أستخدم نموذج اعادة معايرة الذرة الحرة (RFA) لدراسة الترتيب الالكتروني لمركب كاربيد الفناديوم (VC).حيث تم ايجاد قيم التراتيب الالكترونية لكل من الكاربون و الفناديوم على انفراد ثم قمنا باستخدام نموذج التركيب الاعظم (Superposition) لحساب منحني كومبتون الكلي للمركب. هذه القيم تمت مقارنتها مع ما متوفر من قيم عمليه لآخرين وباستخدام طاقه عالية (661.65 keV) لاشعة كاما المنبعثة من مصدر السيزيوم ^{137}Cs . حيث لا حظنا امرين وهما الاول; في حال تركيز نصف كثافة الزخم الالكترونية في الفاناديوم داخل المركب سوف نحصل على الترتيب الالكتروني الاتي $(2s^{1}-2p^{1.5})C+(3d^{+5.5}-4s^{1})$. اما الامر الثاني هو في حال تركز كل الكثافة الالكتروني في عنصر الفاناديوم داخل المركب نحصل على الترتيب الالكتروني الاتي $(3d^{7}-4s^{1})V+(2s^{1}-2p^{0})C$. ان افضل النتائج التي حصلنا عليها هي عند انتقال كل الالكترونات من الكاربون الى الفاناديوم.