مجلة جامعة تشرين للدراسات والبحوث العلمية _ سلسلة العلوم الأساسية المجلد (25) العدد (13)2003
Tishreen University Journal for Studies and Scientific Research- Basic Science Series Vol (25) No (13) 2003

Estimation of the KLL Auger Transition Probability in P and Na of the Na_3PO_4 Compound by means of Hydrogenic Model

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(Accepted 13/10/2003)

☐ ABSTRACT ☐

This paper aims at studying KLL Auger transitions in P and Na of the Na_3PO_4 compound and estimating the Auger transition probability with the help of hydrogenic model.

This paper contains comparison between the following quantities: Auger transition probabilities, transition shifts and their intensities represented by area of peak in the spectrum for P and Na. We found a reciprocal relation between shifts for both elements mentioned above.

It is known that phosphorus is a constituent in various semiconductors, for example, InP, GaP, AlP ….etc which have widely practical applications.

On the one hand, studying changes of the Auger transition energies between compound and element – the chemical shift- points out the shift orientation of the density of electrons of atoms inside compound.

On the other hand, the contaminants C,N and O existed on the surface layer of specimen contribute to chemical shifts.

In addition, the Auger transition probability is considered as an important factor for knowing the yield of Auger electrons.

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تقدير احتمال انتقال اوجيه KLL في الفوسفور والصوديوم من المركب Na_3PO_4 بوساطة النموذج الهيدروجيني

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(قبل للنشر في 2003/10/13)

□ الملخّص □

يهدف هذا العمل إلى دراسة انتقالات اوجيه من النوع KLL في ذرتي الفوسفور والصوديوم من المركب Na_3PO_4، وتقدير احتمال هذا الانتقال بمساعدة النموذج الهيدروجيني.

ويحتوي هذا العمل على مقارنة بين احتمال انتقالات اوجيه وانزياحاتها، وشدتها المعّبر عنها بالمساحة الواقعة تحت القمة في الطيف المأخوذ للفوسفور والصوديوم. ولقد وجدنا علاقة عكسية بين انزياحات انتقالات اوجيه لكلا العنصرين المذكورين أعلاه. وتأتي أهمية هذا من حقيقة أن الفوسفور يدخل في العديد من أشباه النواقل مثل InP, GaP, AlP... الخ التي لها تطبيقات عملية واسعة.

إن دراسة تغيير طاقة انتقال اوجيه بين المركب والعنصر أو ما يدعى بالانزياح الكيميائي تشير إلى اتجاه انزياح كثافة الإلكترونات للذرة داخل المركب، هذا من جهة.

ومن جهة أخرى، تساهم الشوائب C, N, O الموجودة على الطبقة السطحية للعينة في عملية الانزياح الكيميائي.

علاوة على ذلك، يعتبر احتمال انتقال اوجيه عاملاً مهماً في معرفة مردود إلكترونات اوجيه.

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1.Introduction:

X- ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) are widely used in qualitative and quantitative studies of surfaces and interfaces.

AES is a relatively new analytical technique which provides qualitative and quantitative analysis of the elements presented in the first fewer atomic layers of a specimen surface [1].

The aims of this paper is to study the KLL Auger transitions in phosphorus as it is a constituent in various semiconductors, for example, InP, GaP, AlP ….etc[2,3].

Such semiconductors have important applications in optoelectronics[4].

1.1. KLL – Auger Transitions

When a primary beam of photons of energy ħω is incident upon the surface of a specimen, its interaction with the surface atom may result in removing an electron from, say the K shell, and the atom will be raised from its ground state figure 1.

If another electron from a higher energy level, say L_1, falls into vacancy created in the K shell, then the atom must release some energy equal to the differences in binding energies between these two levels, i.e. $E_K – E_{L1}$.

The energy difference can either be emitted as a X – ray quantum or transferred to another electron in a higher level, say L_2 which, if it has sufficient energy, may escape from the atom called an Auger electron.

The $L_1L_2M_1$ transition, containing an initial hole which is filled by an electron from the same shell but different sub shell, is called the Coster – Kronig transition.

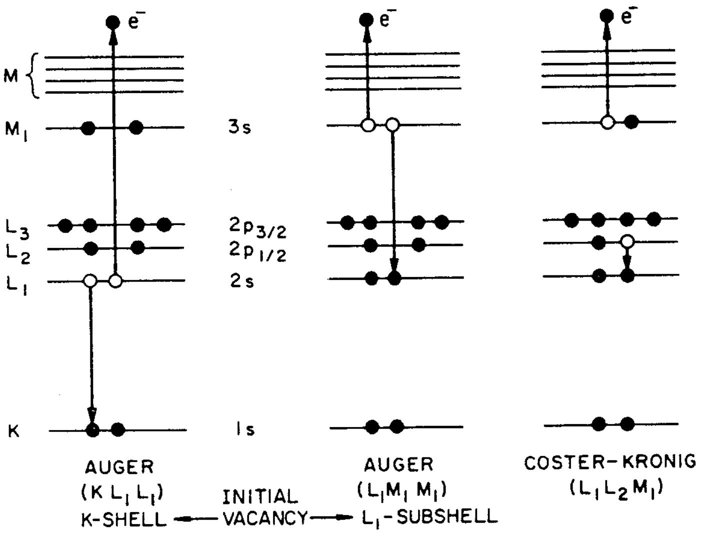

Fig. 1: Mechanism of the Auger Process

The energy of the Auger electron can be determined by the differences of the total energies before and after the transition. An empirical way of doing that is by [5]

$$E_{abg}^{Z} = E_{a}^{Z} - E_{b}^{Z} - E_{g}^{Z} - \frac{1}{2}\left[\left(E_{g}^{Z+1} - E_{g}^{Z}\right) + \left(E_{b}^{Z+1} - E_{b}^{Z}\right)\right] \qquad (1)$$

where E_{abg}^{Z} is the Auger energy of the transition αβγ of the element Z

The first three terms correspond to the difference in the binding energies of shells α,β,γ of the element Z. The last term involves the average of the increase in binding energy of the γ-electron when a β- electron is removed and of the β- electron when γ-electron is removed [6].

In the hydrogenic model the kinetic energy of the KLL Auger electron E_A is given by

$$E_A = E_{KL2L2} = E_K - E_{L2} - E_{L2} = E_K/2 \qquad (2)$$

$$ak = (a_0 / Z)\sqrt{mE_{Kin} / \mathbf{h}^2} = 1/\sqrt{2} \qquad (3)$$

where E_{Kin} the kinetic energy of a electron, the radius related to Bohr radius as $a = a_o / Z$, k wave number of electron and the terms on the right hands of eq.(2) are the binding energies according to the hydrogenic model given as following:

$$E_n = E_0 Z^2 / n^2 \ ; \ E_0 = 13.6 \text{ eV} \qquad (4)$$

1.2. The Transition Probability

In this calculation we are considering a KL_2L_2 transition which takes place from 2p state (L_2) to the 1s state (K) and the subsequent emission of another 2p electron (L_2) as a free electron.

The transition probability W per unit time from the initial state i to the final state f is given by [7]

$$W = \frac{2\pi}{\hbar} D(k) \left| \langle \psi_f | H | \psi_i \rangle \right|^2 \qquad (5)$$

$$D(k) = m(V/8\pi^3\hbar^2) k \sin\theta \, d\theta \, d\Phi \qquad (6)$$

where D(k) is the density of states associated with normalization in a box of volume V, m and k are mass and wave number of electron, H is the perturbation potential of the electron – electron interactions.

1.2.1. Evaluation of the Transition Probability for $E_{K\alpha}$ Emission

Based on eq.(5) we get the Transition formula for $E_{K\alpha}$ Emission:

$$W = \frac{4}{3} \frac{e^2}{\hbar} \left(\frac{\hbar \omega_{fi}}{\hbar c} \right)^3 \left| \langle \psi_f | r | \psi_i \rangle \right|^2 \qquad (7)$$

where $\hbar\omega_{fi}$ is the energy of the emitted photon, Ψ_i and Ψ_f are the wave functions of the initial and final states and $\langle \psi_f | r | \psi_i \rangle$ is the dipole moment.

For Ψ_i and Ψ_f we will use hydrogenic wave functions table 1.

Table 1: Hydrogenic wave function, $\rho = r/a$ and $a = a_o/Z$ [8]

n	**l**	**m**	**R_{nl} (r)**	**Y_{lm} (θ,Φ)**
1	0	0	$\frac{2}{a^{3/2}} e^{-\rho}$	$\frac{1}{\sqrt{4\pi}}$
2	0	0	$\frac{1}{4}\left(\frac{2}{a^3}\right)^{1/2} (2-\rho) e^{-\rho/2}$	$\frac{1}{\sqrt{4\pi}}$
2	1	0	$\frac{1}{4}\left(\frac{1}{2\pi}\right)^{1/2} \left(\frac{1}{a}\right)^{3/2} \rho e^{-\rho/2}$	$\sqrt{\frac{3}{4\pi}} \cos\theta$

2	1	±1	$\frac{1}{4}\left(\frac{1}{2\pi}\right)^{1/2}\left(\frac{1}{a}\right)^{3/2} r\, e^{-r/2}$	$\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}$

$$\Psi_f = \Psi_{1s} = R_{10}(r)\, Y_{0,0}(\theta,\Phi) \qquad (8)$$

$$\Psi_i = \Psi_{2p} = (1/\sqrt{3})\, R_{21}(r)\, [Y_{1,0}(\theta,\Phi) + Y_{1,-1}(\theta,\Phi) + Y_{1,1}(\theta,\Phi)\,] \quad (9)$$

Using spherical coordinates as

$$\langle\psi_f|r|\psi_i\rangle = \langle\psi_f|r\sin\theta\cos\phi|\psi_i\rangle + \langle\psi_f|r\sin\theta\sin\phi|\psi_i\rangle + \langle\psi_f|r\cos\theta|\psi_i\rangle \quad (10)$$

The wave functions Ψ_f, Ψ_i have a finite intensity only for values of $|r| \le a$.

Substituting wave functions in eq.(10) yielding:

$$\langle\psi_{1s}|r|\psi_{2p}\rangle \sim a \qquad (11)$$

On the other hand, the energy of the transition 2p→ 1s in hydrogenic model is

$$\hbar\omega = E_0\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)Z^2 = 10.2Z^2 \qquad (12)$$

With help of eqs.(7,11,12) we find that the transition probability is proportional to Z^4. Thus we rewrite W in the unit of eV/ħ as

$$W_X = 7.10^{-10}\, (\hbar\omega)^3 / Z^2 \quad (13)$$

1.2.2. The KLL Auger Transition Probability in a Hydrogenlike Atom

The transition probability W_A for the Auger effect can be written as

$$W_A = \frac{2\pi}{\hbar} D(k)\left|\varphi_f(r_1)\psi_f(r_2)\frac{e^2}{|r_1 - r_2|}\varphi_i(r_1)\psi_i(r_2)dr_1dr_2\right|^2 \qquad (14)$$

For the KLL transition there are two steps: the first one is the 2p→ 1s initial process and the second step is the 2p → free Auger electron as final process.

The free Auger electron can be considered as an outgoing plane wave.

Then, for convenience it is useful to write the wave functions (see Tab.1)for KLL Auger transition as function of r/a.

$$\varphi_i(r_1) = \varphi_{2p}(r_1) = \frac{1}{\sqrt{6a^3}}\varphi'_i\left(\frac{r_1}{a}\right) \qquad (15)$$

$$\phi_f(r_1)=\phi_{1s}(r_1)=\frac{2}{\sqrt{a^3}}\phi_f'\left(\frac{r_1}{a}\right) \qquad (16)$$

$$\psi_i(r_2)=\psi_{2p}(r_2)=\frac{1}{\sqrt{6a^3}}\psi_i'\left(\frac{r_2}{a}\right) \qquad (17)$$

$$\psi_f(r_2)=\frac{1}{\sqrt{V}}e^{iak.r_2/a}=\frac{1}{\sqrt{V}}e^{ir_2\cos\theta_2/a} \qquad (18)$$

The potential can be written as

$$\frac{e^2}{a}\left(\frac{1}{|r_1/a-r_2/a|}\right)=\frac{e^2}{a}V'(r_1/a-r_2/a) \qquad (19)$$

Based on the fact that the radial extension of the 1s wave function is small in comparison with the 2p function and in the crude approximation $r_2>r_1$ we get

$$\frac{1}{|r_2-r_1|}\cong\left[1+\left(\frac{r_1}{r_2}\right)\cos(\theta_2-\theta_1)\right] \qquad (20)$$

Substituting eq.s (15 – 20) into eq.(14) we get

$$W_A=\frac{2\pi}{\hbar}\frac{mkd\Omega}{8\pi^3\hbar^2}\frac{ae^4}{9}F \qquad (21)$$

where dΩ = sinθdθdΦ

$$F=\left|\iint\frac{dr_1}{a^3}\frac{dr_2}{a^3}\phi_f'\left(\frac{r_1}{a}\right)\psi_f'\left(\frac{r_2}{a}\right)V'\left(\frac{r_1}{a},\frac{r_2}{a}\right)\phi_i'\left(\frac{r_1}{a}\right)\psi_i'\left(\frac{r_2}{a}\right)\right|^2 \qquad (22)$$

where F is a definite integration over all space for r_2/a and $r_{1/}a$.

Taking dΩ = 4π and ak = 1/√2 the eq.(21) can be written as

$$W_A = \frac{me^4}{9\sqrt{2}\pi\hbar^3} F = C\frac{me^4}{\hbar^3} \qquad (23)$$

where C is a numerical constant. It is to notice that the ratio of the Bohr velocity v_0 to the Bohr radius a_0 is equal to $me^4/\hbar^3$ which is the inverse of the characteristic atomic time $a_0/v_0 = 2.4\times10^{-17}$ s.

The result for W_A is independent of Z in contrast to the strong Z dependence of radiative transitions W_X for K_α emission.

BURHOP [8] has suggested a semi empirical relation for the atomic fluorescence yield ω_x of the form

$$\omega_X = (W_X/W_A)/(1+ W_X/W_A) \qquad (24)$$

so that the Auger electron yield is

$$\omega_A = 1- \omega_X \qquad (25)$$

$$W_X/W_A = 10^{-8}.(-6.4 + 3.4Z - 1.03Z^3)^4 \qquad (26)$$

2. Experimental

The spectrum of Na_3PO_4 was achieved at Leipzig University – Germany and the theoretical study at Tishreen University – Lattakia.

The experimental data were taken by a vacuum generator ESCA – (electron spectroscopy for chemical analysis) electron spectrometer working with CHA – (cylindrical hemispheric analyzer) in the constant pass energy 50 ev figures 2,3.

During the XPS/XAES measurements the specimen was irradiated with Ag $L_{\alpha1}$(2984.3ev) and Al Kα(1486.6ev) [9].

Photoelectron lines and X- ray excited Auger electron lines occurring in the XPS spectra as seen in figure 3, where O_{1s} is photoelectron peak for oxygen.

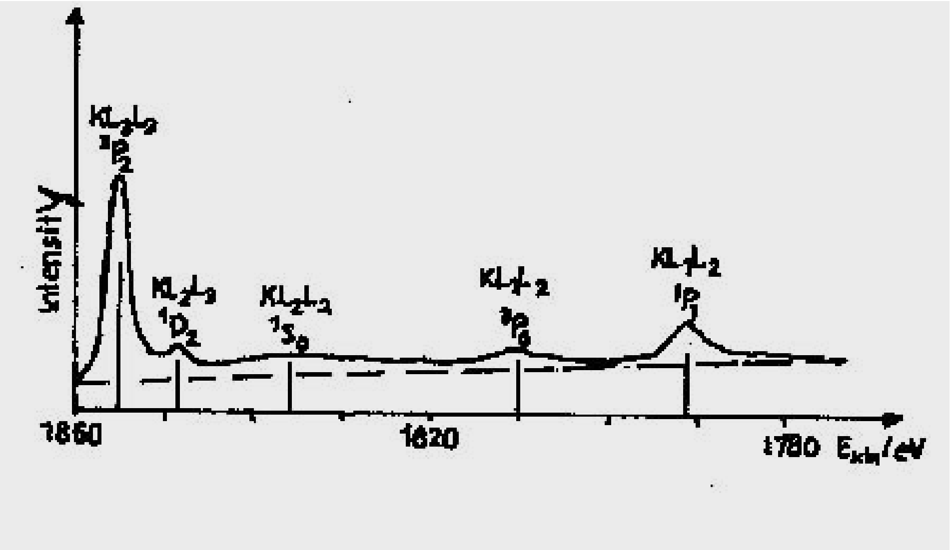

Fig. 2: The KLL transition in P of sample Na_3PO_4

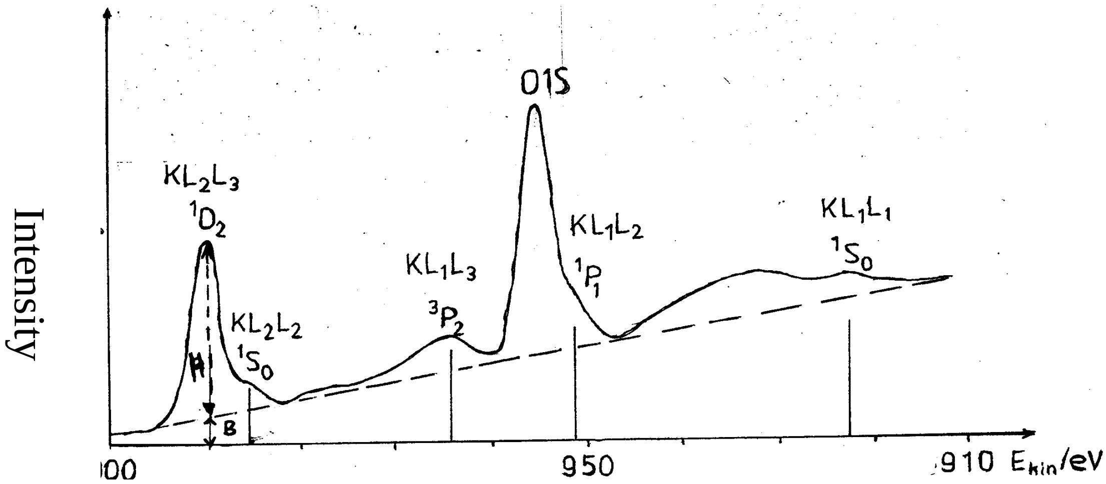

Fig. 3: The KLL transition in Na of sample Na_3PO_4

In the spectrum the peak area A represents the quantitative analysis. It is usually done by multiplying the peak height at maximum P_{max} with the peak width at half height w_h, assuming that the peak is Gaussian in shape [10].

$$A = P_{max} \cdot w_h \qquad (27)$$

There is a relationship between w_h and the peak width at base w_b[10].

$$w_b = 1.699\, w_h \quad (28)$$

Another approach for measuring the intensity [11, 12] is to calculate the peak to background height H/B (see fig.2).

3. Results and Discussion

We registered in table 2 the electron binding energies for following elements Na, Mg, P, S.

Table 2:All values are given in eV [13]

elements	**K**	**L_1**	**L_2**	**L_3**
Na	1072	63	31	31
Mg	1305	89	52	52
P	2149	189	136	135
S	2472	229	165	164

Table 3 contains the transition rates which are calculated from eqs.(13,26).

In addition we tabulated the numerical constant C whose value represents the integral F eq.(23).

Table 3: Transition rate for E_α emission, Auger transition and the numerical constant, calculated with help of eqs.(13, 23,26). E_α values taken from [13].

P (Z=15)				**Na (Z=11)**			
E_α(eV)	**W_X(eV/ħ)**	**W_A(eV/ħ)**	**C_P**	**E_α(eV)**	**W_X(eV/ħ)**	**W_A(eV/ħ)**	**C_{Na}**
2010	0.025	0.65	55´ 10^{-3}	1040	0.007	0.71	50×10^{-3}

The Auger transition energies of P and Na in Na_3PO_4 which are extracted from figures 2and 3 are registered in tables 4 and 5.

Table 4: Auger transition energies of P (values in eV), D- Auger energy shifts referred to element P ; (H/B) ratio and peak area A extracted from figure 2 with help of eq.(27)

sample	$^1P_1$ KL_1L_2	$^3P_0$ KL_1L_2	$^1S_0$ KL_2L_2	$^1D_2$ KL_2L_3	$^3P_2$ KL_3L_3
P^*	1784	1805	1835	1845	1852
P^{**}	1789.5	1789.5	1848	1849	1850
P in Na_3PO_4	1790.76	1810	1831.92	1845.38	1855
D_P	6.76	5	-3.08	0.38	3
$(H/B)_P$	0.62	0.16	0.14	0.5	6.75
A_P(a.u)	35.3	7.35	8.82	10.59	190.62

* Taken from [13]

** calculated from eq.(1)

Table 5: Auger transition energies of Na (values in eV), D- Auger energy shifts referred to element Na ; (H/B) ratio and peak area A extracted from figure 3 with help of eq.(27).

sample	$^1S_0$ KL_1L_1	$^1P_1$ KL_1L_2	$^3P_2$ KL_1L_3	$^1S_0$ KL_2L_2	$^1D_2$ KL_2L_3
Na^*	928	952	967	984	989
Na^{**}	920	954.5	954.5	989	989
Na in Na_3PO_4	922.5	951.53	964.23	985.38	990
D_{Na}	-5.5	-0.47	-2.77	1.38	1
$(H/B)_{Na}$	0.068	0.61	0.33	0.83	6.6
A_{Na}(a.u)	7.06	84.15	64.7	35.3	388.41

* taken from [13]

** calculated from eq.(1)

From figures 2 and 3 we notice that KL_3L_3 and KL_2L_3 Auger transitions are highest in intensity since electron – electron interactions are strongest between electrons whose orbitals are closet together.

The phosphorus atom in Na_3PO_4 is surrounded by four oxygen atoms as first environment and as second circumstance surrounded by sodium ions.

The chemical environment of an atom is reflected in changes in the valence shell orbitals which in turn influence the atomic potential and the binding energy of the core electrons. The binding energies of the inner core K and L shell shift in unison with changes in the chemical environment. For this reason we correlate D_P for KL_2L_3, KL_1L_2, KL_2L_2 – transitions with counterparts D_{Na} in figure 4.
It is noticed from fig.4 a reciprocal relation between both shifts.

Tables 4 and 5 contains experimental Auger transition energies of P and Na as individual elements and as in compound. The salient differences between values may be ascribed to the extra atomic relaxation energy term expecting in compounds, but values in the second row of both tables calculated by substituting experimental data in approximation relation eq.(1) in which the hole-hole interaction energy is ignored.

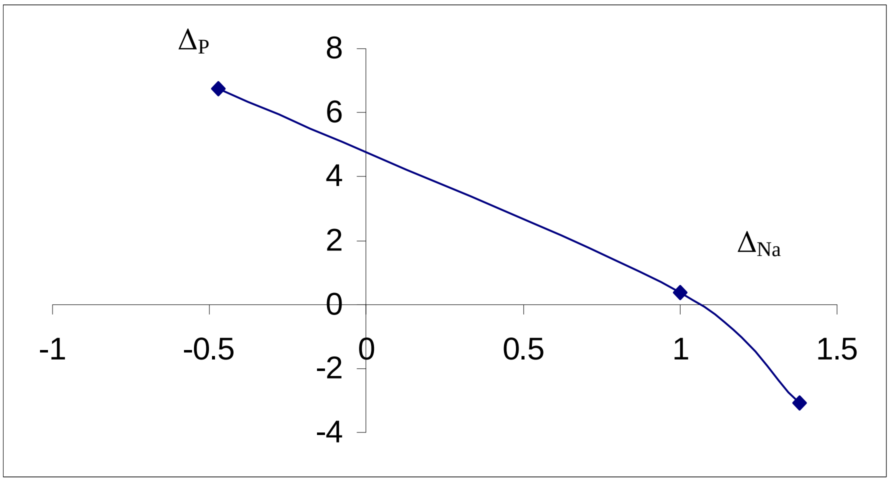

Fig. 4: Comparison of P- shifts with Na – shifts

On the other hand, we compare peak to background ratio and peak area of phosphorus with their counterpart of sodium figures 5 and 6.

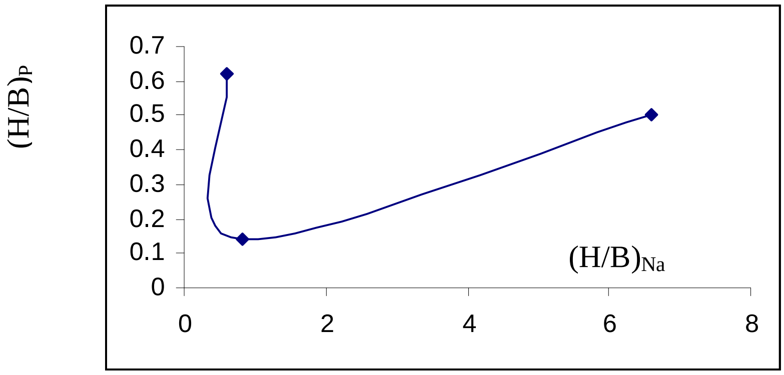

Fig.5:Comparision between $(H/B)_P$ and $(H/B)_{Na}$

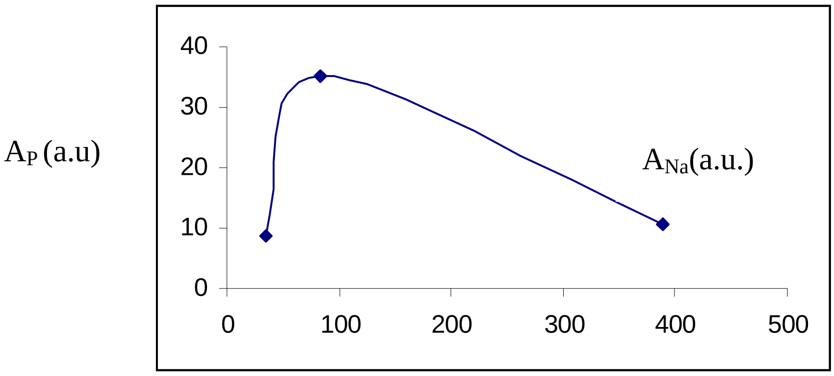

Fig.6:Comparision between peak areas A_P with A_{Na}

We could infer from figures 5 and 6 that the ratio (H/B) is a differentiated form of peak area A.

As conclusion, on one side we demonstrate in this work the experimental results of KLL Auger energies and on the other side we estimate the same results based on the hydrogenic model as a crude approximation.

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