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Lecture

Historical Auger Electron Spectroscopy. I
Works of P. Auger and other pioneers .

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Preface

I was given a chance to review the historical Auger electron spectroscopy and it is a great pleasure to introduce Professor Pierre Auger (4 May 1899 - 24 December 1993) in Photo 1, which presented to the special issue of Journal[1] by J.P.Briand. His work has been performed in his elaborated cloud chamber and constituted his doctoral thesis on 26 July 1926, University of Paris[2]. It may be a nice opportunity to see the results. Then, thus, I dare to show the fantastic photographs as many as possible, (Photo 2), which are revealing really the true nature of the Auger electrons (see also Fig.3 in the text). Auger's bibliography[1], Conferences[3], lectures[4,5] and peaceful humanity[6], have been introduced elsewhere. This review is mainly from a chapter 1, Introduction of my doctoral thesis (Osaka University, 1981). This thesis had unexpectedly been read by Pierre Auger and was greatly appreciated. It might be a dream.

I. Auger's work

Auger electron spectroscopy (AES) was pioneered by Pierre Auger. Although his work was performed in the early 1920's, the results are always so up to date and instructive that one cannot describe AES without mentioning his observation of Auger electrons by his naked eye followed by excellent experimental confirmation. This review describes the historical aspects of AES to figure out basic problems of AES as applied to surface analysis.

1.1. Auger electron spectroscopy (AES) – Its principle and historical background

The Auger effect (named after Auger) was conclusively studied by Pierre Auger through use of a cloud chamber, an improve type of the chamber invented by Wilson (1911)[7] and (1912)[8] (Fig.6). This research

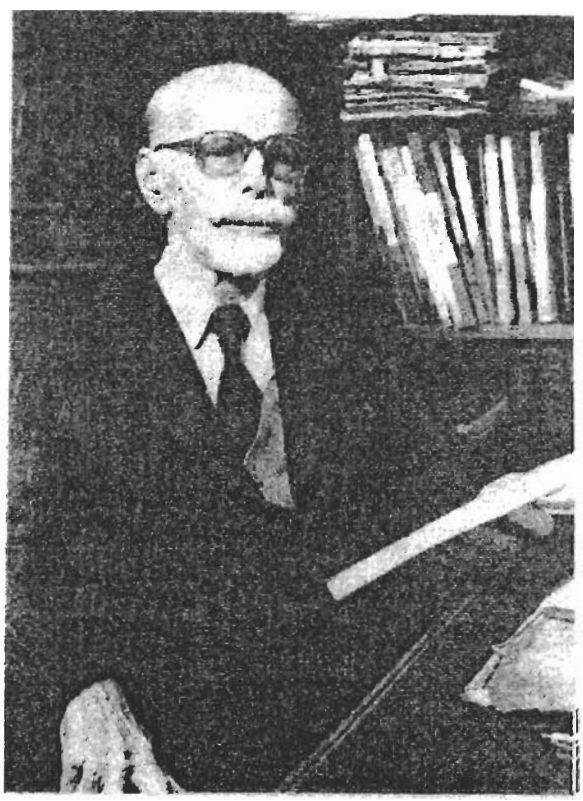

Photo 1. Pierre Auger (4 May 1899 – 24 December 1993) (Ref.1) (courtesy of JEOL).

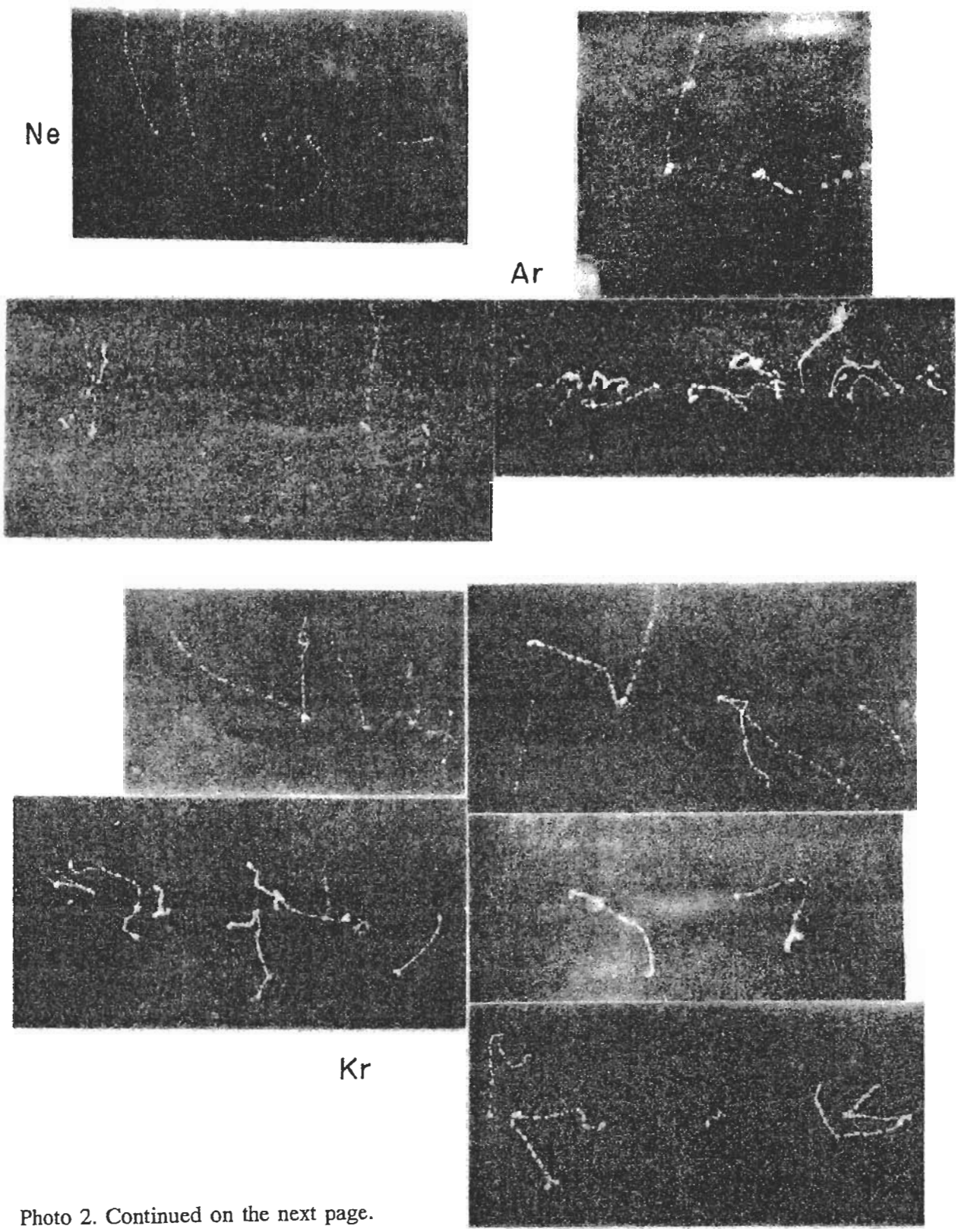

Photo 2. Continued on the next page.

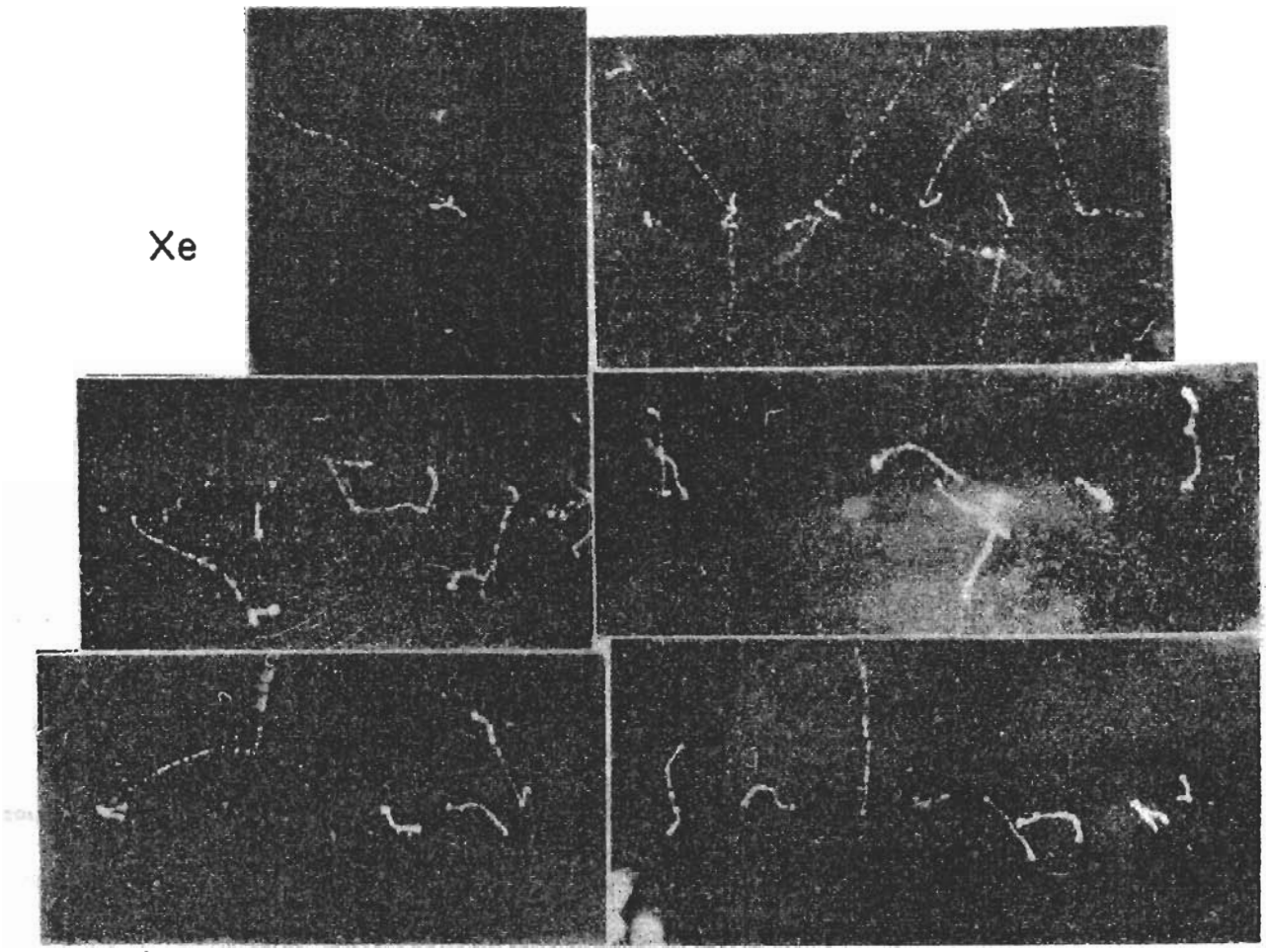

Photo 2. Traces of photo– and Auger–electrons in the cloud chamber; Ne, Ar, Kr, and Xe (Ref.11).

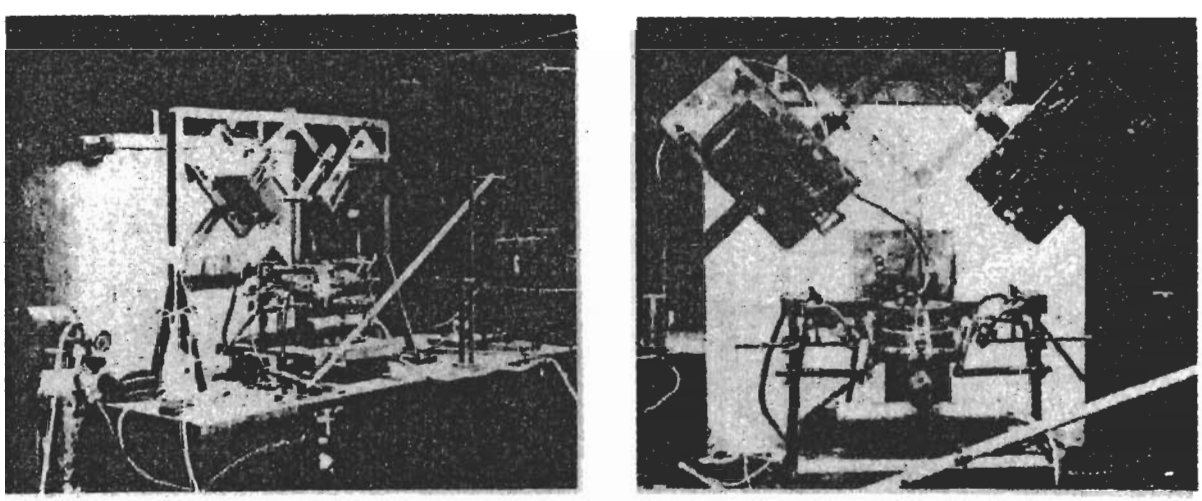

Fig.1. Original experimental arrangement of the cloud chamber used by Auger for the discovery of Auger electrons, by Auger (1926) (Ref.11).

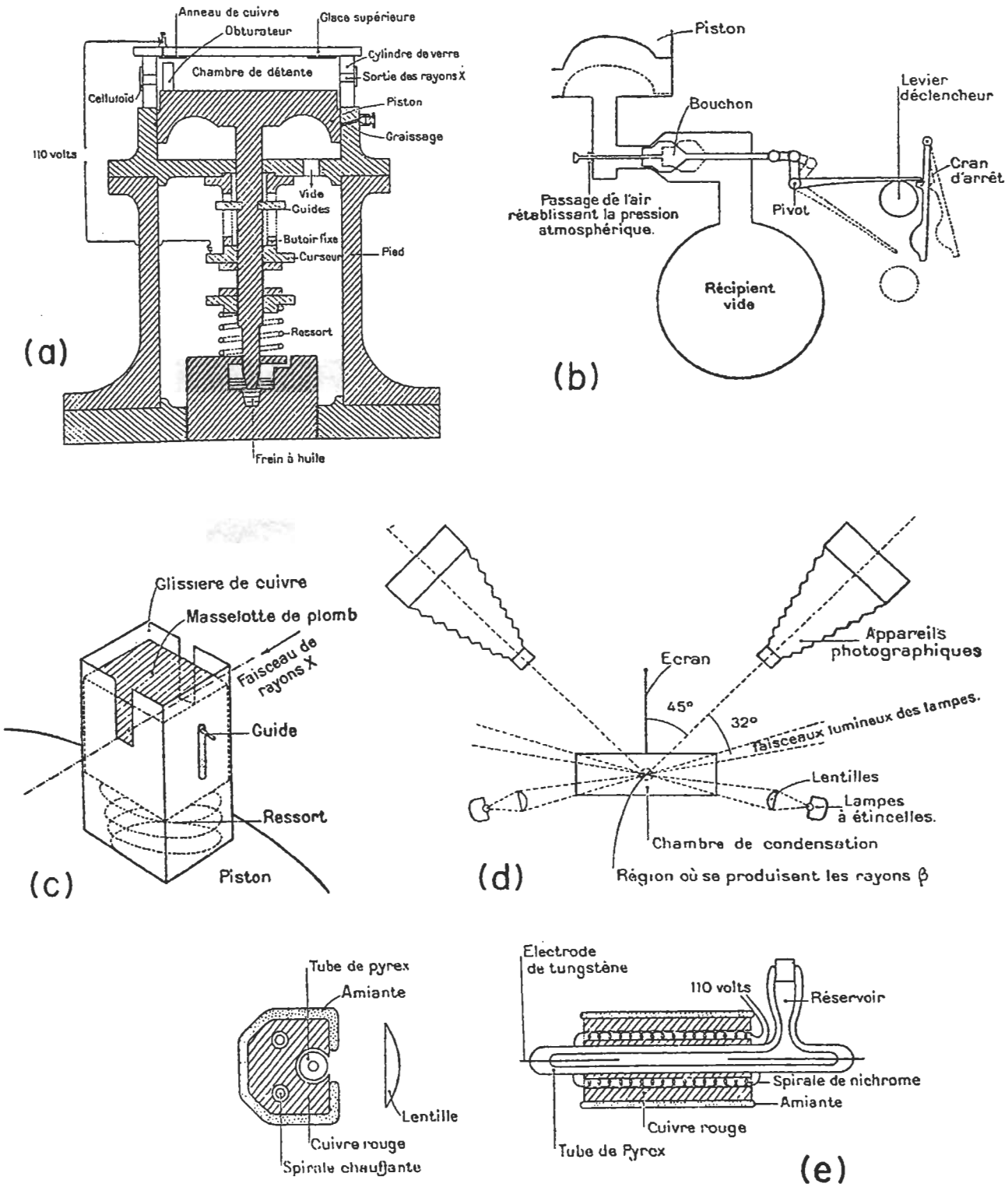

Fig.2. Details of the experimental arrangements, (a) cloud chamber, (b) expansion mechanism, (c) shutter for X-rays "synchronized" to the expansion, (d) photographic arrangement, (e) light source by mercury vapor discharge, by Auger (1926) (Ref.11).

began during his study of photoelectric effects by X-rays when he was a graduate student at the Ecole Normale Superieure. This research was further developed by him in the laboratory of Professor Jean Perrin[1-5].

His first note on the observation of the Auger effect for N_2, Ar, Cl_2 and I_2 was published in 1923[9] and for N_2, Ar, I_2, Kr and mixture of air in 1925[10]. His elaborate apparatus[11] used are shown in Fig.1 and Fig.2 where the photographs in Ref.5 seem to be "negatives". To make the effects clearer, he used a short-pulsed X-ray source of 20-100keV, which was roughly monochromatized using proper filters to select appropriate photon energies as the primary beam. As shown in Fig.2, the beam was collimated to be a narrow beam of 0.5mm in diameter (d). He also examined the use of a crystal to monochromatize the beam. Then the tracks pulse-lighted by vaporized mercury lamps (e) in the cloud chamber (a) were photographed with two cameras set out at 45° from surface normal (d). All these processes were mechanically synchronized, ((b) and (c)). This arrangement allowed him to measure lengths of the tracks with considerable accuracy leading to better quantitative study.

In the chamber, sample gases of N_2, Ne, Cl_2, Ar, Br_2 and Xe were used. Gases of $CHCl_3$, CCl_4, CH_3I, CH_2Br_2, CO_2 and I_2 were not suitable because they reacted with wet H_2 gas under the light, which made many seeds of cloud. These gases were diluted by wet H_2 gas to be 2-10% in order to lengthen the tracks. This dilution reflects Auger's excellent sense of experiment.

Typical electron tracks[5,11,12] are shown in Fig.3*. Auger defined a photoelectron produced directly by the incident X-rays as the secondary electron, electrons excited by the first Auger effect as tertiary electrons, those by the second Auger effect as fourth electrons, and so on. Fig.3(a) was obtained for Ar (5% in H_2), excited by X-rays of 45keV. The long tracks were photoelectrons and shorter ones (~1mm, seen as a heap) were Auger electrons (*KLL*, ~3.2keV). In Fig.3(b), far left, a photoelectron track, and Auger electron (*KLL*) and a pair of Auger electrons (*LMM*) ejected by X-rays of 90keV for Xe (2% in H_2) are shown.

The energies of the ejected electron were roughly estimated using the Whiddington's law, thus the obtained value would include considerable ambiguity. Although this was a drawback of this method, the obtained values showed fairly close agreement with a theoretical value estimated from the other methods assuming the Auger process. The minimum observable energy was 800eV for Ne(*KLL*) which corresponded to the length of the track of only a fraction of a millimeter.

Thus, Auger obtained the following important experimental results:

1. The length of the tracks (tertiary and fourth electrons) were independent of the incident primary radiation (X-rays) energies.
2. The photoelectrons and tertiary (fourth, ...) electrons were generated at the same origin.
3. The heavier the weight of atom, the longer became the length of the track of the tertiary (Auger) electrons and vice versa.
4. The spatial distribution of the photoelectrons had a maximum in the plane

*Incidentally, the photograph of Fig.4 in Ref.5 seems to be miscited (see Refs.11 and 12). Caption of the photograph should be 3% Kr in H_2 by 60keV of X-rays.

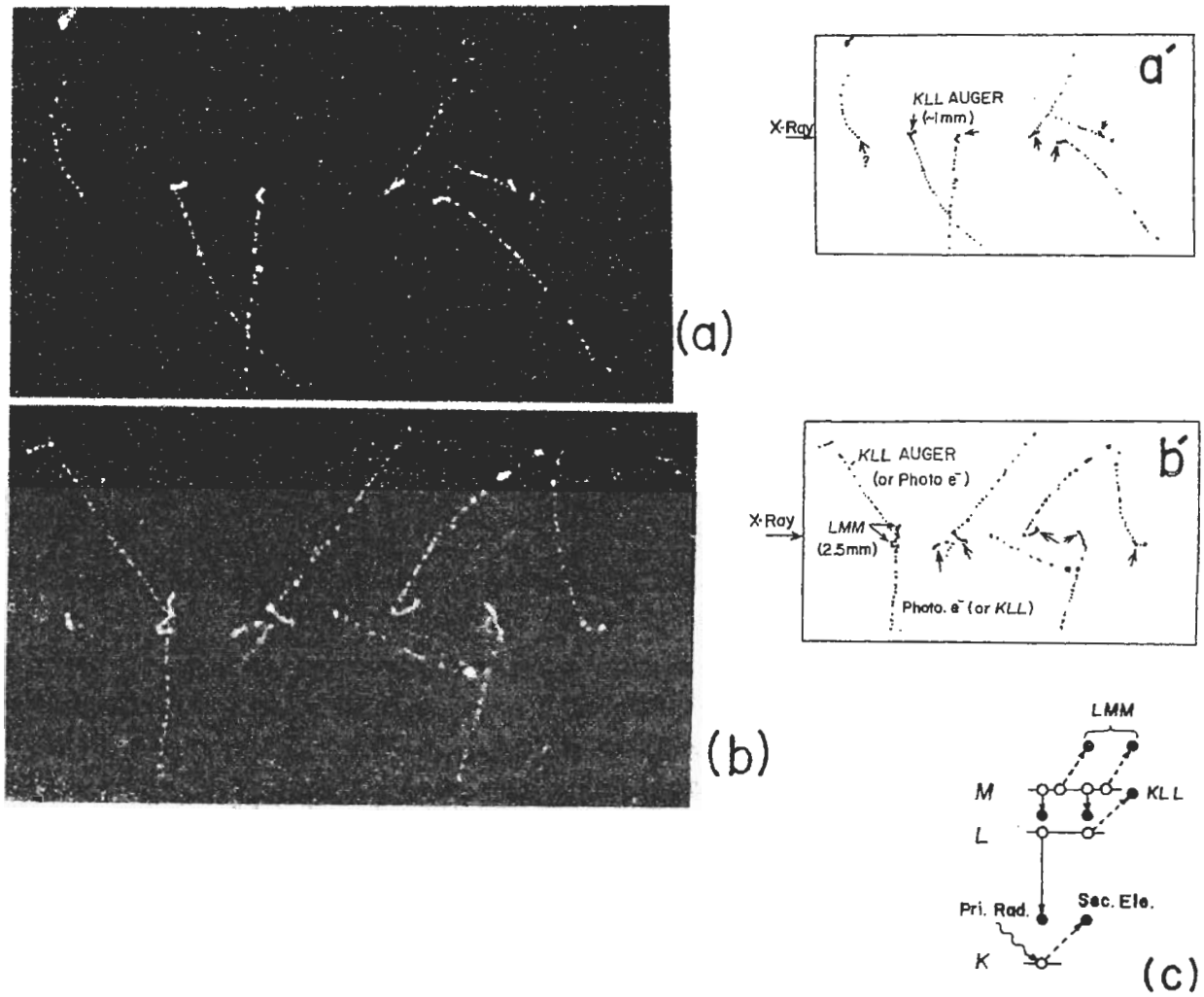

Fig.3. Typical electron tracks (Auger- and photo-electrons) excited by X-rays of (a) 45keV and (b) 90keV in 5% Ar in H_2 and 2% Xe in H_2, respectively (Ref.12). (a') and (b') correspond to (a) and (b), respectively, with the notation of the tracks (by the author). (c) is a schematic illustration of the possibility of one *KLL* and two *LMM* Auger electron emission. This example is shown in the far left in (b) and (b').

of the electric vector of the incident photons, while that of the Auger electrons was isotropic.

5. The probability of the Auger electron excitation was considerably scattered probably because of the statistical properties.

6. The lighter atoms were more effective in producing the Auger electrons than the heavier ones.

From those experimental results Auger successfully figured out the following model which explained the results, i.e., "Auger transition". The model is schematically illustrated in Fig.4 to explain the Auger transition as follows:

1. One of the incident X-ray quantum with energy E_p ejected the *K*-shell electron, to which the incident quantum energy was completely transferred. This *K*-shell electron ejected was called a photoelectron (secondary electron) with energy of $E_p - E_K$.

2. The vacancy in the *K*-shell was filled up

by a L–shell electron. Then, the electron liberated an energy of $E_K - E_L$. There were two ways to liberate this energy.

3. The radiation emitted from the atom was called K–fluorescence with the characteristic energy of $E_K - E_L$. This is an intermediate stage of the process shown in Fig.4(b) which will be discussed later.

4. On the contrary, as a complementary effect of the fluorescence, the another L–shell electron was ejected with an energy $E_K - 2E_L$ by the reabsorption in the same atom of the quantum of energy liberated in process (2) in Fig.4(a). The ejected L–shell electrons is called a *KLL* Auger electrons. Auger said that this implied *some kind of internal conversion of potential energy into mechanical energy* instead of producing an electromagnetic quantum.

5. Further, the two vacancies in the L–shell would be filled up in the same way as is described above, i.e., fluorescence of L with energy $E_K - E_M$ or Auger electrons of *LMM* with energy $E_K - 2E_M$. The last example is schematically shown in Fig.3(c) and Fig.3(b) and (b'). There would exist variety of the processes between the fluorescence and the Auger. These processes make multiple vacancies in the atom. Auger observed up to 32 positive charges[4]. These facts lead the Auger process to be quite a complicated phenomenon.

6. A process, shown in Fig.4(b) with the fluorescence process as an intermediate stage, could be considered as the probability of this process, however, the orders of magnitude are smaller compared with the Auger process (Fig.4(a)) since there are no tracks originating out of the primary beam. This process seems to yield the same result as the Auger process though the detailed observation of the energy distribution of the ejected electrons by the other authors showed difference between them.

7. The fluorescence yield, a ratio of the number of fluorescence quantum to the sum of those of fluorescence and Auger, was also determined quantitatively by observing both the tracks of photoelectrons and those of Auger electrons.

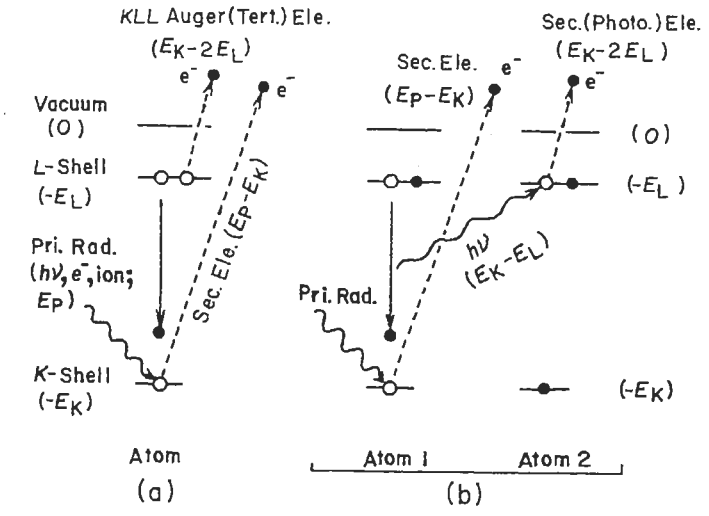

Fig.4. Two possibilities of the observed electron tracks, (a) the internal radiationless transition (i.e., Auger transition) and (b) the K–fluorescence of Atom 1 excites the other Atom 2 as photoelectric effect.

1.2. The Auger- and concerned processes

Klein and Rosseland (1921)[13] proposed theoretically a transition without radiation. They considered a system of collision in thermal equilibrium between electrons (free electrons) and atoms (Bohr-like). They described the model using Einstein's thermodynamical equilibrium between an atomic system and thermal radiation. In the theory, they distinguished the processes of transition into two kinds; the first kind was called the "Franck and Hertz"[14] collision and the second kind was "radiationless". Although the meaning was rather vague, the Auger transition was explicitly included in the second kind. Rosseland (1923)[15] also applied his model of the second kind transition to the published experimental data, that the characteristic β-ray should be due to the internal radiationless transition of the primary α-, β-, and γ-rays from the nucleus.

De Broglie (1921)[16] observed the energy spectrum of photoelectrons from metals due to X-rays. He measured the energy spectrum in detail using a magnetic energy analyzer developed by Robinson and Rawlinson[17]. The original analyzer[17], as shown in Fig.5, was of a second order focusing type and the spectrum was recorded on a photographic plate with an accuracy better than 1%. Using this type of energy analyzer De Broglie performed experiments as follows:

1. Spectra from metals of Zn, Sr(sulfide), Mo(acid), Rh(chloride), Ag, Sn, Sb(sulfide), I(Pb), Ba(oxide) and Y(oxide) were observed.
2. The photoelectrons due to an excitation of the characteristic fluorescence of the substrate were measured for samples, i.e., Ag on PbI, Ag on Ba, Cu on Ba, Cu on Sn, and Cu on Ag.
3. Finally, he used the characteristic X-rays of Rh as the primary beam and the photoelectrons ejected by the X-rays from Cu and Se were observed.

In the spectra, spectra corresponding to the energy of $E(K_\alpha) - 2E(L)$ and $E(K_\beta) - 2E(L)$ were found – these being similar to the process illustrated in Fig.4(b). De Broglie, at least in the first experiment, should actually have observed the "Auger electrons" although he did not identified.

Ellis (1922)[18] studied β-ray groups emitted due to γ-rays from the disintegrating radioactive atoms. Before him, Rutherford had already shown that the

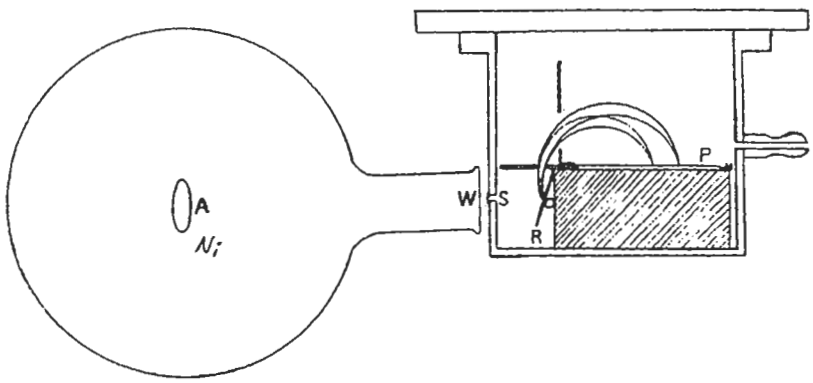

Fig.5. The magnetic energy analyzer by Robinson and Rawlinson (1914) (Ref.17). P; photographic plate, R; radiator, S; thin mica of air tight, W; Al window, A; anode of Ni.

lines in the β-ray spectrum were due to the conversion of monochromatic γ-rays within the same radioactive atom that emitted them, i.e., the photoelectric effect. Ellis, however, extended the idea of Rutherford and assumed that the γ-ray from the nucleus of an atom could be converted to the fluorescence energy (for example the K-line) and then this energy could be transferred to another electron (for example a L-electron) in the atom by internal energy conversion. Subsequently this electron would be emitted as a β-ray (with energy $E_K - E_L - E_L$). This model seems close to that shown in Fig.4(b), but the real process occurs in the same atom. In fact, this model is exactly the same as the Auger process and was proposed before Auger's observation! Ellis explained successfully his experimental results using this model. He also found that the observed energy of β-rays, using a magnetic energy analyzer, shifted toward the lower energy side as compared with the normal atomic energy level by X-ray data. According to his model it was not necessary to use the monochromatic γ-rays for explaining the results but in fact a "white" or a combination of the two could be used. Those facts represented the exact feature of the Auger process.

Ellis (1927)[19] also measured the relative intensities of the groups of the β-ray spectra of radioactive atoms. The combination of the magnetic energy analyzer and a photographic plate were used for quantitative measurements. In the experiment a signal (peak) to noise (background) ratio was typically of a few percent. This made experiments hard to evaluate. The problem of background has been argued for a long time, but it is left unsolved as yet. He obtained a result that the ratio of the intensities for the β-ray groups by the internal energy conversion of γ-rays was independent of the energy of the γ-rays and approximately equal to the cases of the external energy conversion of the γ-rays and X-rays.

Wilson, who had invented the revolutionary cloud chamber[7,8] (Fig.6), also studied how X-rays affect the photoelectric effect for metals, i.e., Cu and Pt, and for the air in the cloud chamber (1923)[20]. The apparatus and the method seem quite similar to Auger's (Fig.2). This is quite natural as the Wilson's was the original prototype. Wilson observed many "paired" electrons in the cloud chamber. A typical result obtained for the air is shown in Fig.7, in which two tracks are shown. By using stereo-photography, we can see the fantastic feature of the nature stereographically by adjusting eyes. Looking at Fig.7, two long tracks and two "fish" (seen as fish-tails) can be found. The latter should denote Auger electrons. Similar tracks other than the "fish" such as "spheres" and "commas" depending on their shape were also observed. Almost all of these should be Auger electrons. Wilson explained the results assuming a process like Fig.4(b). In the cause of his research, he had practically arrived at the same results as Auger though he did not completely determine the process. The primary X-rays used were far from homogeneous and the length of the tracks (fish, sphere and comma) were too short to determine the energy with considerable accuracy.

Robinson (1926)[21] studied the secondary and tertiary electrons ejected by Mo K_α and Cu K_α X-rays, using his improved magnetic energy analyzer[17] (Fig.5) with an energy

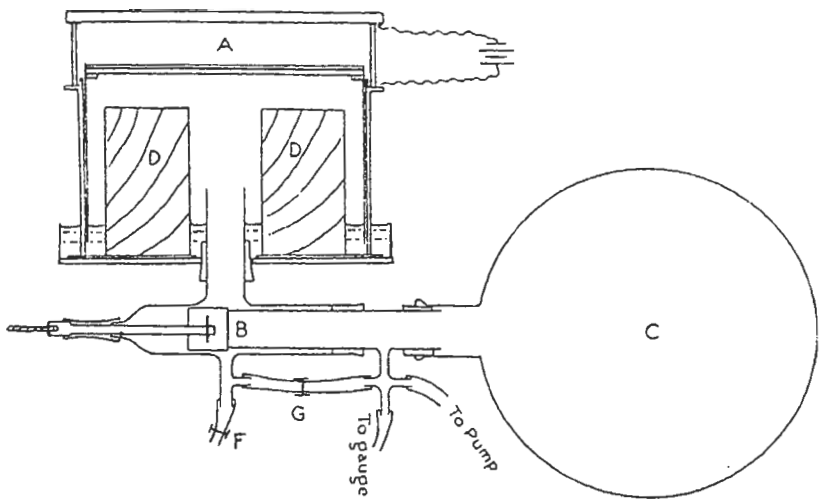

Fig.6. The first cloud chamber by Wilson (1911 and 1912) (Refs.7 and 8). A; the observation space, B; bulb, C; vacuum, D; wooden cylinder to reduce the volume of air.

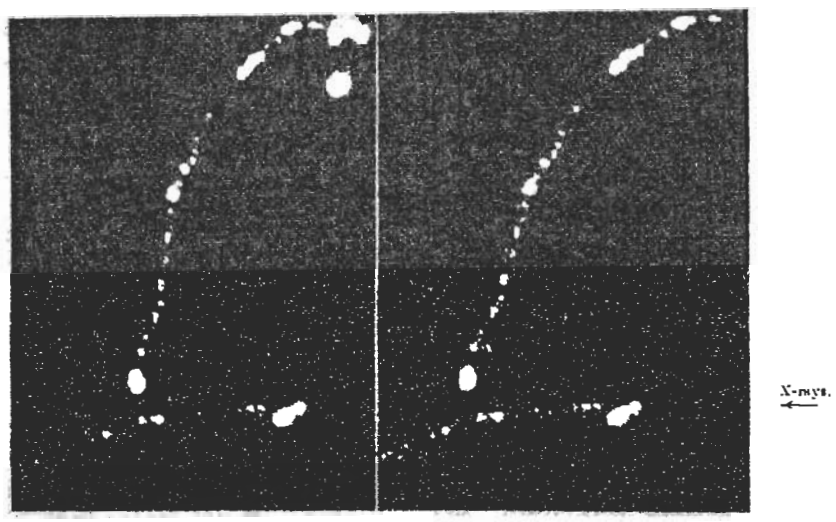

Fig.7. Typical stereoscopic photograph of the cloud chamber by Wilson (1923) (Ref.20). Two paired tracks are shown; long tracks (photoelectrons) and short tracks, seen as heaps, (Auger electrons). Paired tracks seem to be starting at the same points (parentheses by the author).

resolution, $\Delta E/E$, approximately 10^{-3}. Samples of Ca(sulphate), Cu, As(oxide), Br(ammonium bromide), Zr(oxide), Mo, Ag, Ba(carbonate), Ce(oxide), W(oxide), Au, Bi(oxide), Th(nitrate) and U(oxide) were used, in which Cu was extensively studied. Summing up the results, he clearly concluded, based on the data from Cu, that the tertiary electrons must be ejected by the internal conversion of the energy through a "radiationless" process[13,15] (Fig.4(a)), since the observed energy value always shifted towards the lower side. This can be explained by the fact that the vacancy in the atom, which is doubly ionized, makes the energy level somewhat deeper. The secondary electrons by the external excitation by the Cu K_α X-rays were also observed, but the resulting energy values were those deduced from the atom at the normal state. Further, the probability of the external excitation was too faint to be observed for the very thin samples used.

Robinson and Young (1930)[22] also reported the details of the energy spectra for the materials mentioned above. It should be noted that they predicted the use of their method, i.e., the energy analysis of the tertiary (Auger) electrons, for a determination of the elements. Today, this method is known as *Auger electron spectroscopy* (AES). Robinson and Young argued that their method was the most direct method available and to be free from many of the difficulties which appeared in the X-ray spectroscopy of the corresponding emission lines. They also worried about the intense continuous background as Ellis[19] did.

Concerning the vacancies in the atomic shells due to the quantum absorption, Wentzel (1921)[23] calculated the energy shift of the shells theoretically. Wentzel (1927)[24] first calculated theoretically the Auger process using wave mechanics. He calculated a ratio of Auger yield to that of the fluorescence for the K-ionization. As a result, the value would be proportional to

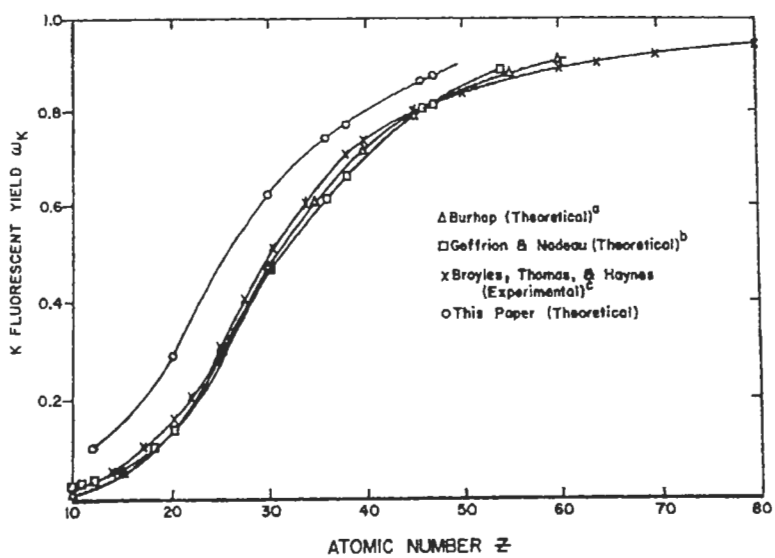

Fig.8. The computed and experimental K-shell fluorescence yield curves by Callan (1961) (Ref.27).

the value between Z^{-4} to Z^{-3}, where Z is an atomic number. This value showed fairly close agreement with those derived by Auger[11]. In the same year as Wentzel (1927), Fues (1927)[25] also obtained theoretically similar results using wave mechanics.

Asaad and Burhop (1958)[26] calculated the positions and relative intensities of the *KLL* and *KLM* Auger lines for different atomic numbers (Z=29 to 83), with electron energies of 6keV to 74keV, based on a non-relativistic treatment assuming an intermediate coupling. They obtained quantitative agreement between the theoretical prediction and experimental data.

More recently, Callan (1961)[27] computed *KLL* Auger transition probability for atoms of atomic number 10 to 80, using screened non-relativistic hydrogenic wave functions, with screening constants derived from results of the Hartree-Fock self-consistent-field functions. The computed results are compared in Fig.8 with results from other authors.

A Coster-Kronig transition (1935)[28] is also a kind of Auger process, a specific type such as found in *LLM* transition. Coster and Kronig explained the experimental results successfully based on theories of charge densities of levels and the overlapping of wave functions.

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Comments and Replies
/Reviewer : T. Sekine (JEOL)

Q1: In 1922, Ellis proposed the model for the radiationless transition, which is very similar to or the exact same model as that we call "Auger effect," from the study of β-ray emission due to γ-rays. This is almost one year earlier than the first publication
for the Auger effect by P. Auger in 1923. People recognize today that P. Auger is the man who discovered it. How do you interpret for the difference of appreciation between those works?

Author : My description is correct as Prof. Auger has appreciated (Private communication).

Q2: P. Auger conducted experiments with cloud chamber but Ellis did with electron spectrometer. And, P. Auger studied gases but Ellis studied solids. From this article I understand the excellency of P. Auger as an experimental scientist, and at the same time I sense that he was lucky, in terms of discovery of Auger effect, because he did not suffer surface contaminations while Ellis might have suffered for there were no concept of UHV in those days.
Do you have any comment for it?

Author : I quite agree with you. Either scientist was lucky as Auger dealt with rare gases and Ellis dealt with very high energies γ – and β - rays. These two types of experiments were immune from contaminations!

編集者から；著者から査読者への回答にはコメントが上記の他に日本語でつけられていました．とても興味深いものなのでここに掲載します．（著者了解済み）文責：編集委員会

Q1 -> A1; ご質問の通りで，私も実は困って，これが詳しく調べる基になりました．でも，歴史的にはこれで正しいようです．学位論文を書くに当たり，もしこの項がオージェ先生のお気に触れて世界のヒンシュクを買ったら私は以後オージェ電子の仕事をしないつもりでいました．ところが，オージェ先生は立派です！　その通りでEXACTだとお手紙をくださいました．そのときの感激　おわかりになりますか？

したがってかどうかは，わからないのですが，オージェ電子という言葉が使われるようになったのはずいぶん後になってです．たぶん1953年のJ.J. Landerが始めて使ったと思うのですが．他の分野（原子核，宇宙線）は調べていませんのでわかりませんが，この分野にあると思われます．（オージェ先生はこちらの方に入っていますので）．このような事情は2回目に知っている範囲で述べます．

学位論文（大阪大学，1981年）をオージェ先生にご紹介くださったのはC. LeGressus氏で，私がまだ下書きを書いているときから「おもしろい！仕上がったら3部送ってくれ（仏に），1部はオージェ先生に渡すから」といってくれていたので９９％冗談とはおもいつつも，約束だから3部送りました．ところが，本当にオージェ先生にお渡しくださったようです．その日はちょうどノーベル物理学賞発表の日で，Siegbahnがそれに決まったと報道された日です．オージェ先生はこの決定にひどく不快を示されていたらしく「あんな．．．」と不機嫌だったようです．そこで，LeGressus氏は戸惑いつつソッと私の学位論文を机上において様子をうかがっていたら，夫人が「日本のムッシューが．．．」と言葉を添えてくれたということです．以後は聞いていませんが，しばらくしてお手紙（(Nov.2, 1981付け，１４年前の今日）を戴くわけです．

オージェ先生はご親戚に，キュリー夫妻子息，J.ペラン（義理の父），ランジュバン．．．などそうそうたる方々が居られ，人脈にも通じていたと思われるのですがノーベル賞をもらわなかったのは（運動は８０年代～９０年代にあったが），査読者の問われるオリジナリティーにあるのではないでしょうか．一説には２０年代の仕事を今頃ということもあるでしょうし，また，この（Auger effect）仕事を続けておられれば簡単だったともいわれているようです．でも，Auger先生にとっては先

生の仕事はあれで十分終わっていることではないでしょうか．　いいですねこういうのは，先生は恐らくこう言われていたのではないでしょうか，「これ以上一体何をやればいいと言うのかね，十分にきれいな結果だし，この写真を美しいとは思わないかね．私にとってはもう終わったことだ．Ellis や Wentzel も既にやっているし，Willson もイギリスで私と同じ結果を発表しようとしているらしいし，私にはたいしてオリジナリティーはないよ．あとはやりたい人がやってくれ．ただし，やることは山程あるよ！」とおっしゃっていたような気がします．

以上，私案もまじえて Legressus 氏よりうかがったところです．Auger 先生ご自身ノーベル賞にこだわったかどうかは知りません．大して興味を示されなかったのではないでしょうか．ただし，周りの人々が望んだのではないかと思います．