

«ESCA, a new experimental approach to understanding of chemistry»(*)

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Refere-se a importância que a ESCA tem no estudo de estruturas químicas e expõe-se resumidamente o fundamento do método ESCA, apresentando-se espectros do óxido de magnésio, cloreto de sódio, etc., obtidos por este processo.

Estudam-se algumas aplicações do método ESCA, com particular relevância para a investigação da natureza das ligações químicas, mostrando-se a partir da equação de Schrödinger que as riscas do espectro ESCA, correspondentes a órbitas electrónicas internas, são muito sensíveis à natureza dessa ligação.

Conclui-se fazendo referência a possíveis desenvolvimentos tecnológicos da ESCA.

Since I am a physicist and the title of my talk contains the word chemistry, I should like to start with some general remarks about chemistry. I realized that the students of physics in our physics department usually hate chemistry or, at least, are afraid of chemistry, and I should like to analyze why this is the case.

I believe that the reason is the fact that still today a large fraction of chemical research is done in the chemistry laboratories just by mixing together some strange materials in the oldfashioned way and observing what happens. I oversimplify now, but one has indeed accumulated a tremendous knowledge about chemical reactions and compounds and their physical and chemical properties in a completely empirical way.

Modern physics and modern quantum mechanics, especially, has lead to an understanding of the atom and to a complete understanding of the chemical bond; in principle everything about chemistry could be calculated and predicted now; only the complexity of the subject is the reason, why up to now «computer chemistry» played only a minor role. The exact calculation of the electronic orbitals in large molecules and the derivation of all physical and chemical properties of these molecules from the shape of these orbitals is still an unsolved computer problem.

In this situation the direct experimen-

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tal investigation of electronic orbitals has a tremendous importance.

A few tools are well-known, the most important ones being electron spin resonance (ESR) and Mössbauer spectroscopy. ESCA is quite a new additional tool for microscopic investigations which promises to contribute a lot to the understanding of chemical structures in solid or gaseous substances.

Let me start with a short description of the principle of ESCA. The word ESCA is the abbreviation of electron spectroscopy for chemical analysis. This name is somewhat misleading because it neither characterizes the experimental technique sufficiently nor describes the most important field of applications. The principle is explained schematically in fig. 1. The characteristic radiation of an X-ray tube hits a probe and photo-absorp-

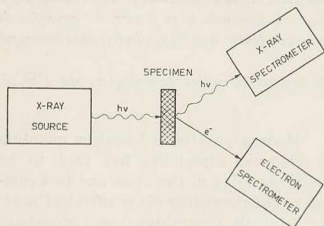


Fig. 1 — Schematic diagram illustrating the principles of X-ray spectroscopy and ESCA.

tion processes take place. The X-ray fluorescence as well as X-ray absorption spectra can be investigated by the well-known X-ray spectroscopy techniques. A similar information could be obtained, however, by observing the energy spectra of the primarily emitted photoelectrons. The kinetic energy of the photoelectrons is determined by the photoelectric equation:

$$E_{\text{kin}}(e^-) = h \cdot \nu - BE(e^-)$$

The binding energies BE of electrons are shown schematically in form of an X-ray level scheme in fig. 2.

The discussion which we made here is more than fifty years old. The scien-

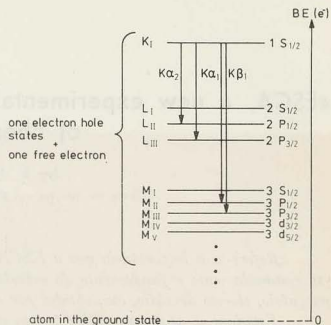


Fig. 2 — X-ray level scheme.

tific world believed for about fifty years, however, that only the X-ray spectroscopy is a valuable method whereas the photoelectron spectroscopy seemed not to be feasible because of inelastic scattering processes of the electrons on their way through the target. The nuclear physicists have developed electron spectroscopy especially for the study of the energies of conversion electrons. These conversion lines show always a long tail on the low energy side, which is produced by energy losses of the electrons by many excitation and scattering processes in the source material. The cross-section for these processes is so large that a tail is observed even if extremely thin sources are used. Fig. 3a shows as an example a conversion electron spectrum, which was measured in our laboratory about ten years ago in the decay of lutetium 177m; the spectrum was taken with a

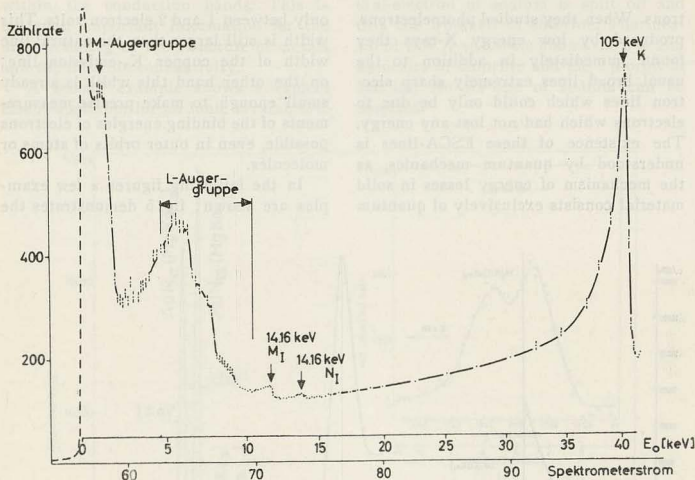


Fig. 3a — Conversion electron spectrum of ^{177m}Lu between 0 and 40 keV. This figure is taken from ref. 1.

double focussing magnetic spectrometer. The tail on the left side of the 105 keV K-conversion line is typical. Fig. 3a shows in addition two interesting low energy conversion lines between 10 and 15 keV. They are shown on a larger scale in fig. 3b. When we had observed these spectra we had some discussions about the shape of these lines. Especially for the 14.16 keV M_I -line we observed that the last points on the right-hand side of the peak were higher than expected. If the resolution of our spectrometer would have been a little better we probably would have realized that there was a sharp extra-line of electrons which had not lost any energy when passing through the source material.

These extra lines, the so called ESCA-

-lines, were first observed by K. Siegbahn and coworkers in Uppsala. This group had developed especially high resolution spectrometers (2) (3) for low energy elec-

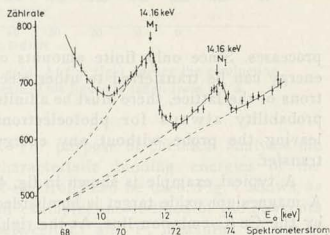


Fig. 3b — Conversion lines between 10 and 15 keV of the spectrum of fig. 3a in an enlarged scale.

trons. When they studied photoelectrons, produced by low energy X-rays they found immediately in addition to the usual broad lines extremely sharp electron lines which could only be due to electrons which had not lost any energy. The existence of these ESCA-lines is understood by quantum mechanics, as the mechanism of energy losses in solid material consists exclusively of quantum

only between 1 and 2 electron volts. This width is still larger than the natural line width of the copper K_{α} -emission line; on the other hand this width is already small enough to make precise measurements of the binding energies of electrons possible, even in outer orbits of atoms or molecules.

In the following figures a few examples are shown: fig. 5 demonstrates the

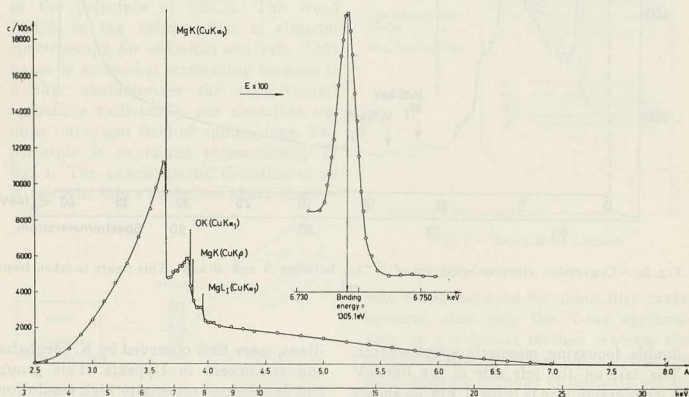


Fig. 4 — Electron spectrum obtained from magnesium oxide with copper X-radiation. This figure is taken from ref. 4.

processes. Since only finite amounts of energy can be transferred to other electrons of the lattice, there must be a finite probability always for photoelectrons leaving the probe without any energy transfer.

A typical example is shown in fig. 4. A magnesium oxide target is bombarded by the $Cu K_{\alpha}$ -emission line. At the right corner of the figure one of the ESCA-lines is plotted at a larger scale. This plot shows that the width of the line is

typical conduction band structure of metals. In this case the target is gold and the photoelectrons are produced by the 1,2536 keV magnesium K_{α} -line. The conduction band has a width of about 10 eV and consists of 5d and 6s electron orbitals. It must be mentioned that it was very difficult before, to get experimental information about the exact position and structure of conduction bands. Precise ESCA-measurements make it possible, now, to derive also the density of states

within the conduction bands. This is quite an important information for the understanding of the structure of metals and the metallic conductivity.

A second example shows a typical ESCA-spectrum for an ionic crystal, i. e.

(3s)-electron of sodium is split off and fills the 3p-shell of chlorine. The measured ESCA-spectrum shows the 3p- and 3s-orbits of chlorine and the 2p-orbit of sodium. No 3s-line of sodium can be detected.

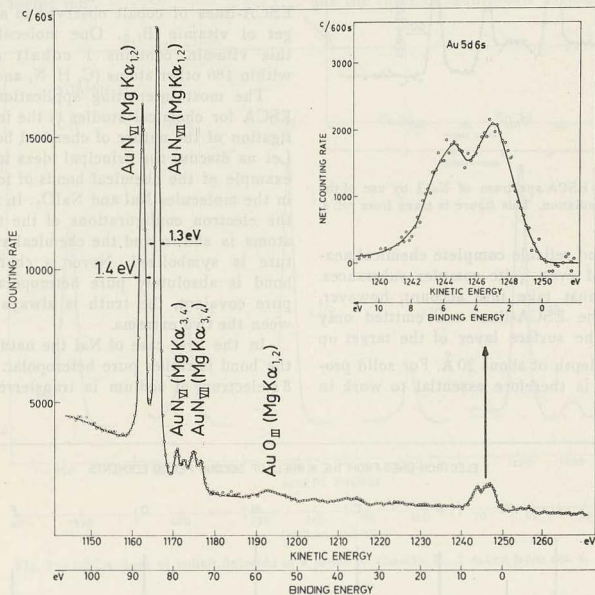
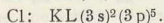
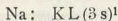


Fig. 5 — ESCA-spectrum of the outer levels of gold. At the right corner the conduction band is shown separately at an enlarged scale. This figure is taken from ref. 4.

NaCl (see fig. 6). The electron configuration of atomic sodium and chlorine are:



In the ionic crystal NaCl the single

For purpose of chemical analysis the characteristic binding energies of the K-electrons can be used. Fig. 7 shows, as an example, the K-lines of the elements between Li and F, measured by use of the aluminum K_{α} -radiation; the nice separation of these intense lines allows an

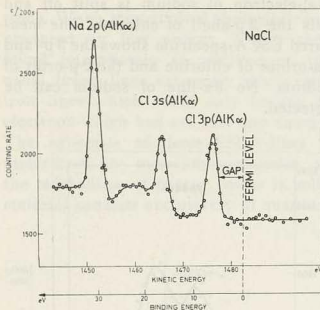


Fig. 6 — ESCA-spectrum of NaCl by use of the Al K α -radiation. This figure is taken from ref. 4.

easy and reliable complete chemical analysis of even quite complex substances. One must take into account, however, that the ESCA-lines are emitted only from the surface layer of the target up to an depth of about 20 Å. For solid probes it is therefore essential to work in

ultra-high vacuum and to apply very careful cleaning procedures in order to get rid of all impurities on the surface of the probe. If sufficient care is applied in the preparation of the target, the ESCA-method is indeed a unique method for chemical analysis. Fig. 8 shows, e. g., ESCA-lines of cobalt observed in a target of vitamin B_{1,2}. One molecule of this vitamin contains 1 cobalt atom within 180 other atoms (C, H, N, and O).

The most interesting applications of ESCA for chemical studies is the investigation of the nature of chemical bonds. Let us discuss the principal ideas in the example of the chemical bonds of iodine in the molecules NaI and NaIO₃. In fig. 9 the electron configurations of the three atoms is shown and the chemical structure is symbolized. Never a chemical bond is absolutely pure heteropolar or pure covalent, the truth is always between the two extrema.

In the first case of NaI the nature of the bond is rather pure heteropolar. The 3s-electron of sodium is transferred to

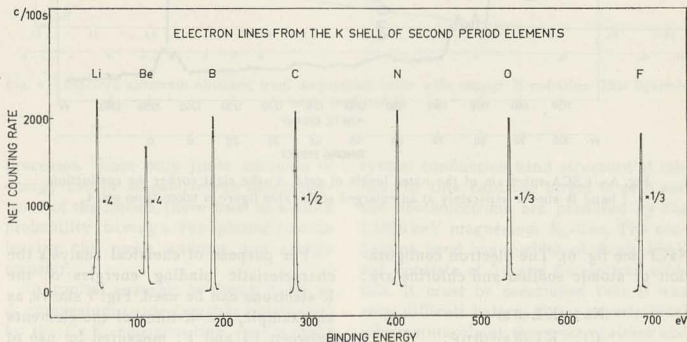


Fig. 7 — K-shell electron lines of light elements produced by the Al K α -radiation. The figure is taken from ref. 4.

the iodine atom and there it fills the 5p shell. By this way two ions with electron shells like those of noble gases are produced. The chemical binding forces are produced by the coulomb attraction between a single positive charge of the sodium ion and a single negative charge of the iodine ion.

2p-shells; this would mean a heteropolar bond between iodine and the oxygen atoms. The other possibility is that these six electrons participate in both atomic shells, i. e. in the iodine (5p)-orbit and the oxygen (2p)-orbit; in the latter case one would call the bond between the iodine and the three oxygen atoms covalent.

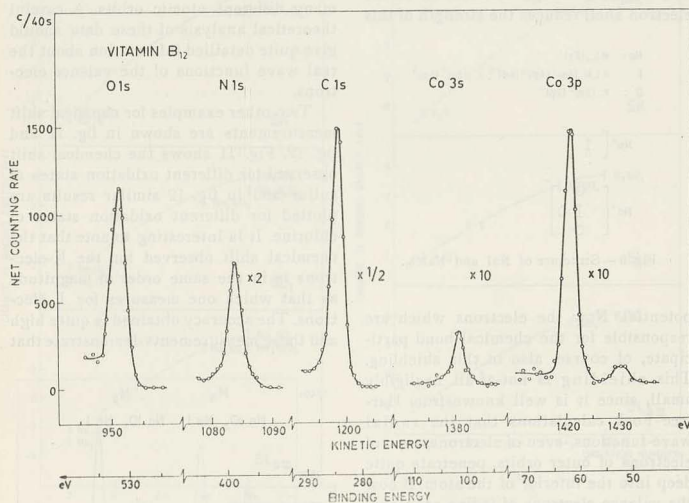


Fig. 8—ESCA lines of cobalt detected in a probe of vitamin B₁₂; taken from ref. 4.

In the second case the sodium-iodate crystal contains a rather pure heteropolar bond between a positive sodium ion and a negative IO₃ ion. The situation for the chemical bond between the iodine atom and the three oxygen atoms, however, is not so clear. The six (5p)-electrons, (including the one which comes from the sodium) could be transferred completely to the oxygen atoms, thus filling their

The ESCA-lines of inner electron orbits are very sensitive to the nature of the chemical bond. This can be understood in the following way:

The eigenfunctions and energy eigenvalues of inner electrons in an atom are the solutions of the Schrödinger equation:

$$\Delta \psi + \frac{2m}{\hbar^2} \cdot (E - V(r)) \cdot \psi = 0.$$

The essential part of this equation is the effective potential energy of the electrons $V(r)$. Without any shielding by the other electrons this potential would be given by:

$$V(r) = -\frac{ze^2}{4\pi\epsilon_0 r}$$

The negative charge distribution of the electron shell reduces the strength of this

- Na: K L.(3s)¹
 I : K L M.(4s)² (4p)⁶ (4d)¹⁰. (5s)² (5p)⁵
 O : K.(2s)² (2p)⁴

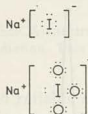


Fig. 9 — Structure of NaI and NaIO₃.

potential. Now the electrons which are responsible for the chemical bond participate, of course, also in this shielding. This shielding is not-at-all negligibly small, since it is well known from Hartree-Fock calculations that the radial wave-functions, even of electrons, of outer orbits, penetrate quite deep into the interior of the atom. If now the valence electrons of iodine are transferred to the oxygen atoms, this shielding is reduced and therefore the binding energy of inner orbitals in iodine is increased. This effect is actually observed for sodium iodate as one can see in fig. 10, where the ESCA M_{IV} - and M_{IV} -electron lines of iodine for an NaI- and NaIO₃-target are shown. The increase of binding energy amounts to about 5 electron volts.

This effect is an example for the so-called chemical shift. Quite a number of chemical shifts investigations have been performed in the past by use of the Mös-

sbaauer effect. In this method the chemical shift is produced by the monopole term of the electric hyperfine interaction with the nuclear charge distribution. The Mössbauer technique is limited to a few suitable Mössbauer nuclei. On the other hand the information obtained by the ESCA-method is more valuable, since chemical shifts can be observed simultaneously for many different atomic orbits. A careful theoretical analysis of these data should give quite detailed information about the real wave functions of the valence electrons.

Two other examples for chemical shift measurements are shown in fig. 11 and fig. 12. Fig. 11 shows the chemical shift observed for different oxidation states of sulfur and in fig. 12 similar results are plotted for different oxidation states of chlorine. It is interesting to note that the chemical shift observed for the K-electrons is in the same order of magnitude as that which one measures for L-electrons. The accuracy obtained is quite high and these measurements demonstrate that

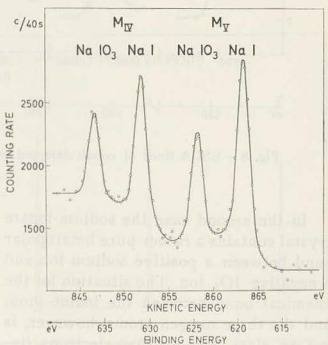


Fig. 10 — Chemical shift of the iodine M_{IV} - and M_{V} -ESCA-lines observed in a mixture of NaIO₃, NaI and NaI. This figure is taken from ref. 4.

the ESCA-technique is indeed a unique tool for chemical structure studies.

Finally I should like to make a few remarks about further technological developments of ESCA. It was shown already,

produced by the continuous X-ray bremsstrahlung-spectrum. An essential improvement is therefore the use of an X-ray monochrometer which selects the interesting characteristic X-ray line out of the

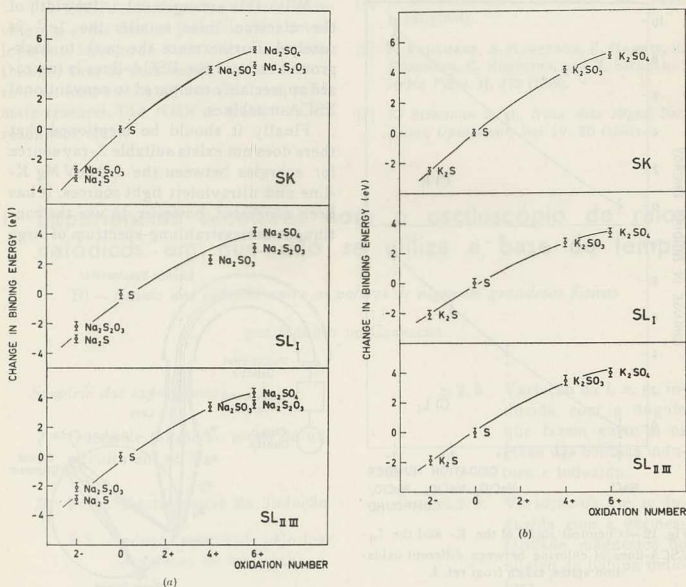


Fig. 11 — Chemical shifts of various sulfur ESCA-lines between different oxidation states, taken from ref. 4.

that the finite width of characteristic X-rays, used for the photoemission process, limits the linewidth observed in the electron spectra. In addition it is sometimes quite a disadvantage that sotelites are observed which are caused by other characteristic X-rays and in addition one has always the background of electrons

background. Fig. 13 shows schematically the construction of a commercial ESCA-machine, built by the firm Hewlett-Packard. This apparatus contains already a bent-crystal X-ray-monochrometer and the following interesting solution was found applied in order to overcome the intensity problem. Instead of selecting

just the inner part of a characteristic X-ray line by use of a small exit slit the whole X-ray line irradiates the target. A system of electric lenses is used to obtain an image of the target at the en-

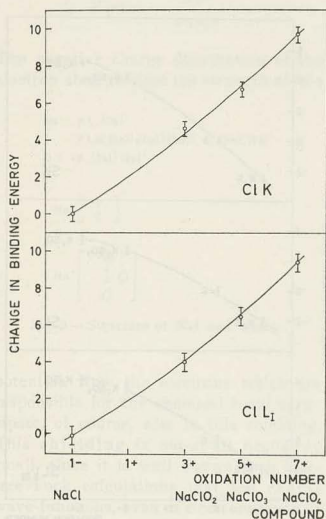


Fig. 12—Chemical shifts of the K- and the L₁-ESCA-lines of chlorine between different oxidation states, taken from ref. 4.

trance of the electrostatic electron-spectrometer. The left-hand side of the target image is that part which was irradiated by X-ray quanta of the low energy side of the X-ray line and on the right hand side the high energy quanta of the X-ray line had emitted the photoelectrons. Now the dispersion of the electron-spectrometer has been adjusted in such a way that all photoelectrons of the same electronic level are focussed to one line at the exit

of the spectrometer. This exit again does not contain a window. Instead a multi-channel-detector system is used which registers simultaneously the whole spectrum. The data are accumulated in a multichannel analyzer.

With this arrangement a linewidth of the electron lines smaller the 1eV is reached. Furthermore the peak to background ratio of the ESCA-lines is increased appreciably compared to conventional ESCA-machines.

Finally it should be mentioned that there does not exist a suitable X-ray source for energies between the 1.2 keV Mg K-line and ultraviolet light sources. It has been suggested, however, to use the continuous bremsstrahlung-spectrum of large

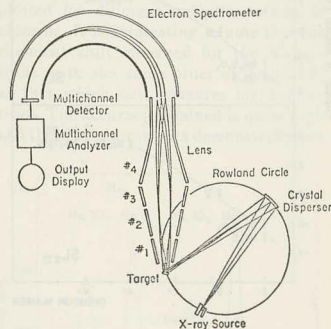


Fig. 13—Sketch of the ESCA-apparatus, constructed by Hewlett-Packard.

electron accelerators for ESCA-purposes. Experiments of this type have been started at the 6 GeV electron-synchrotron in Hamburg as well as at the 2.3 GeV machine at Bonn. Here one can select, in principle, any energy wanted by use of a crystal-monochromator. The main problem is that the intensity is not as high

as one would like to have. Therefore the application of the synchrotron radiation for ESCA-purposes will be limited in the near future at least, to experiments which cannot be performed by conventional X-ray and ultra-violet-light sources.

The ESCA-technique is still in a state where a great deal of technological developments have to be done. One can expect, though, that it will become quite soon a routine instrument of chemical and solid state research like NMR or electron spin resonance etc..

REFERENCES

- [1] E. BODENSTEDT, J. RADELOFF, N. BUTTLER, P. MEYER, L. SCHÄNZLER, M. FORKER, H. F. WAGNER, K. KRIEN, und K. G. PLINGEN; *Z. f. Physik* **190**, 60 (1966).
- [2] K. SIEGBAHN, and K. EDVARSON; *Nucl. Phys.* **1**, 137 (1956).
- [3] A. FAHLMANN, S. HAGSTRÖM, K. HAMRIN, R. NORDBERG, C. NORDLING, and K. SIEGBAHN; *Arkiv Fysik* **31**, 479 (1966).
- [4] K. SIEGBAHN et al., *Nova Acta Regial Soc. Scient. Upsaliensis*, Ser IV, **20** (1967).

I—Experiências escolares com o osciloscópio de raios catódicos em que não se utiliza a base de tempo

B)—Estudo das relações entre os valores de algumas grandezas físicas

por RÓMULO DE CARVALHO

Sumário das experiências:

7. Queda de tensão ao longo de um circuito em série.
8. Força electromotriz de indução.
 - 8.1. Indução provocada pelo deslocamento de um iman.
 - 8.2. Indução provocada por uma bobina percorrida por uma corrente.
 - 8.2.1. Variação da f. e. m. induzida com a intensidade da corrente indutora.
 - 8.2.2. Variação da f. e. m. induzida com o número de espiras da bobina que sofre a indução.
- 8.2.3. Variação da f. e. m. induzida com o ângulo que fazem entre si os eixos das bobinas indutora e induzida.
- 8.2.4. Variação da f. e. m. induzida com a permeabilidade magnética do núcleo da bobina indutora.
9. Estudo das variações do campo magnético criado por uma bobina.
 - 9.1. Influência do número de espiras da bobina sobre o valor do campo magnético criado por ela.
 - 9.2. Influência da intensidade da corrente que percorre a bobina sobre o valor do campo magnético criado por ela.