CRYSTAL STRUCTURES IN THE UNIVERSITY OF BARCELONA. APPLIED SOLUTIONS

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In the area of Barcelona there exists at present four important Centers where different types of X-ray diffraction are carried out. These laboratories belong to the three Universities of the Catalan Government and to the Higher Scientific Research Council (Consejo Superior de Investigaciones Científicas) of the Central Government. They are:

A) University of Barcelona:
- a) Department of Crystallography, Mineralogy and Mineral Deposits;
- b) Scientific Technical Services.

B) Polytechnic University of Catalonia:
- a) Department of Chemical Engineering, Group of Macromolecular Structures.

C) Scientific Research Council of Spain (Consejo Superior de Investigaciones Científicas):
- a) Institute of Material Sciences, Crystal Structure Research Group;
- b) Institute of Earth Sciences (Institute Jaime Almera), Powder X-ray Diffraction Group.

D) Autonomous University of Barcelona:
- a) Department of Geology, Crystal Structure Determination.

In the University of Barcelona X-ray diffraction is in existence in two Departments, the Department of Crystallography, Mineralogy and Mineral Deposits and the Scientific Technical Services. The first is a complex center in the Faculty of Geology created in 1912 as a group to study mine-

rals and general mineralogy; crystallography was necessary to understand mineralogical properties and, in the course of time and as a result of personal efforts, it has become one of the most important parts of the group. Goniometry started in the twenties with the study of the geometrical forms of crystals and, thereafter, their symmetry. In the thirties X-ray diffraction in single crystals was developed with some special studies published in Zeitschrift für Kristallographie. Our Civil War stopped this research for several years and the isolation of our country during the World War and the forties and fifties prevented us from having high-level contacts with world crystallographic science. We wish to recall the difficult times overcome by the effort of Professors F. Pardilla and J. L. Amorós, who worked in Barcelona on crystallography and who were known in the world of our science. Today, the Department is a center with a high level of scientific work.

The second center was created about twenty years ago as a group working in the field of spectrographic analysis; after some time, it was associated with an electron microscope group and was transformed into a scientific technical service of the University. At present it has electron microscope equipment (8 transmission and 3 scanning microscopes with microanalysis accessories), complete modern spectrographic equipment (normal, ultraviolet and infrared), some other special techniques and for the last four years a powder X-ray diffraction group (two Siemens and one Enraft-Intel diffractometers).

The Department of Crystallography, Mineralogy and Mineral Deposits is divided to four research units, as can be seen from figure 1.

A. *Raw Ceramic Materials.* Archaeometry, ceramics and applied mineralogy. UNESCO n.º 331203, 250611, 550599 and 550502.

Research work on the synthesis and process of materials for ceramic use; characterization and application; utilisation of minerals for industry and construction.

B. *Mineral Deposits.* Study and research of the mineral deposits in Catalonia. UNESCO n.º 250610 and 250611.

As-Au mineralization in the Pyrenees (Ordovician) and concentration inside fissures by hydrothermal solution; As-Au and W in hydrothermal concentrations near granite intrusions and metasomatism aureola (skarn) in the Central and Eastern Pyrenees; Pb–Zn–Cu and Mn sulfurs in series of the Lower Carboniferous; Ba–F–Pb–Zn–Ag mineralization associated with pre-Triassic paleosurfaces.

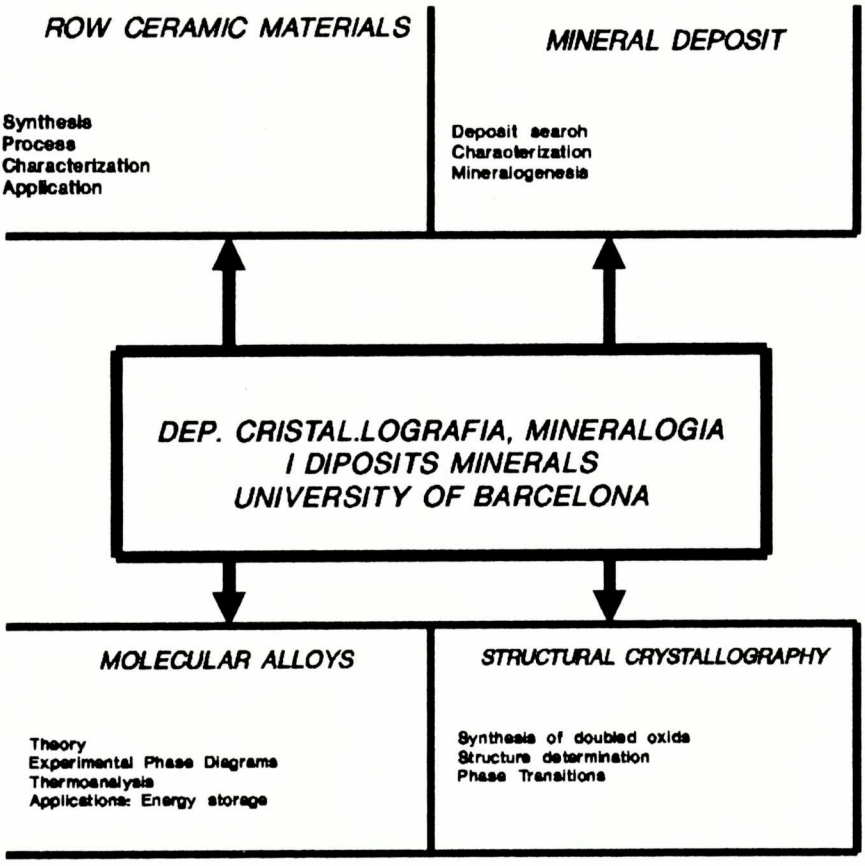

Fig. 1. The schema of the research units in the Department of Crystallography, Mineralogy and Mineral Deposits.

C. *Molecular alloys and isomorphism.* Theory of isomorphism; experimental determination of phase diagrams; forecast, elaboration and characterization of new materials to be used as energy concentrate agents. UNESCO n.º 221104, 221101, 221021, and 332205.

Purifying, crystallographic characterization and the thermodynamics of compounds; creating new molecular alloys by different methods; experimental equilibrium diagrams between phases, theoretical diagrams and relations between them; sincrystallization criterion determination between organic compounds; prototype construction to simulate energy in a real situation; thermal cycles (melting-crystallization) of different weights to obtain the energetic yield of special organic products.

The group collaborates with the Laboratoire de Cristallographie of Bordeaux University and the Thermodynamics Laboratory of Utrecht University; and also with the Department of General Physics of Barcelona University.

D. *Structural crystallography.* Crystal and molecular structure analysis; crystal symmetry; growing crystals in solid state (hexaferrites); phase transitions. UNESCO n.º 221101, 221104, 230326, 230618 and 241599.

Resolution of crystal structures from single crystal X-ray diffraction spectrum; synthesis, crystal growth and structural studies of hexaferrites; scientific support for the X-ray diffraction group of the Scientific and Technical Services of the University; crystal symmetry studies with the goniometer; optics of crystalline compounds and identification of materials by optical methods; n (real) and k determination of light absorbing crystals; microanalysis and identification of layers of paint of wall paintings of 11th to 14th century date and oil and wood ones of 15th to 16th century date.

The main scientific techniques used by the Department are shown schematically in figure 2. X-ray diffraction is the most important method to carry out the wide range of research work with the connection to the general computer of the University and the use of several PC's and microcomputers with crystallographic software of a greater or lesser degree of complexity. Goniometry, optical and electron microscopy, and thermal accessories are basic as complementary methods. A substantial number of different techniques are used in ceramics, thermoanalysis and crystal growth. Mineralogical studies and mineral deposits search have special field methods and laboratory techniques.

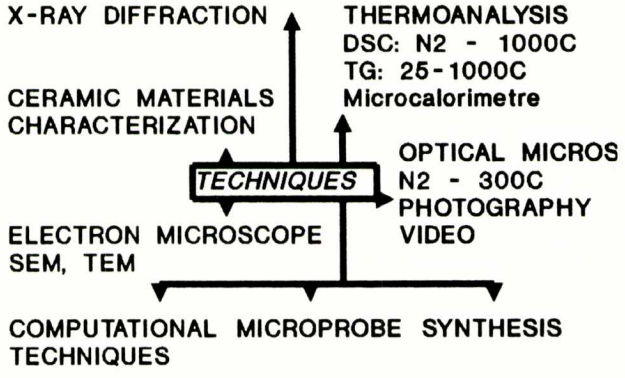

Fig. 2. The schema of main scientific techniques used by the Department.

The Department has two single crystal diffractometers:

a) a PHILIPS 1300 (eleven years old) with low temperature and graphite monochromator; the equipment is ruled by a microcomputer with the corresponding programs to work in a completely automatic form. It was modified to collect data on a PC computer, instead of on the original ribbon system. The programs in the PC computer give us the possibility to correct data for Lorentz-polarization, to reduce the values to an E, and enable us to perform some corrections of absorption.

b) a new ENRAFT-NONIUS CAD4 apparatus, ruled by a microcomputer, with a complete system of software in order to work completely automatically, connected to a series of two PC computers for controling the experimental data. Data from the detector and amplifier are collected on one PC, and they are corrected for Lorents-polarization, any apparatus error detected, and absorption of the parameters of the cyrstal form and symmetry are given. On the other, all corrected data are reduced to an E, and a set of special software permits the calculation of the structure of the sample in some cases (very good crystals, with a small number of atoms), or facilitates work with the corrected experimental data in other fields.

In addition, the Department has other X-ray generators equipped with Weissenberg and Precession cameras, and other special cameras for different types of experiment (Laue research work, twinned crystals, etc.). Figure 3 is the scheme for X-ray diffraction (including the powder diffraction described below).

The research work on crystal and molecular structures which are solved by the apparatus and methods explained, makes use of complementary techniques to establish the morphology and external appearance of the crystals together with their optical properties.

Goniometry was the first method used in the Department to study the morphology of well crystallised minerals, and to stablish habitus of these coming from different origins. A two limbus goniometer of good construction, brought from Germany in 1926, gives angles between faces with ± 1' and, in special cases, ± 30". Calcite, quite abundant in Catalonia, with around 120 habitus described by the Goldschmidt Atlas; Garnets, with different habitus at different local points, differences in morphology connected with their genesis (Sunagawa research works); variation in the position of the surface areas on the same face of a crystal, as in the case of Galena, Quartz, Diamonds, etc.; these were the lines of research followed in the twenties and thirties, together with the study of the morphology of cyrstals going to be examined by X-ray diffraction, which was of assistance because of the need to position the crystal in an exact situation in old X-ray cameras. Today, the goniometer is used to study the ex-

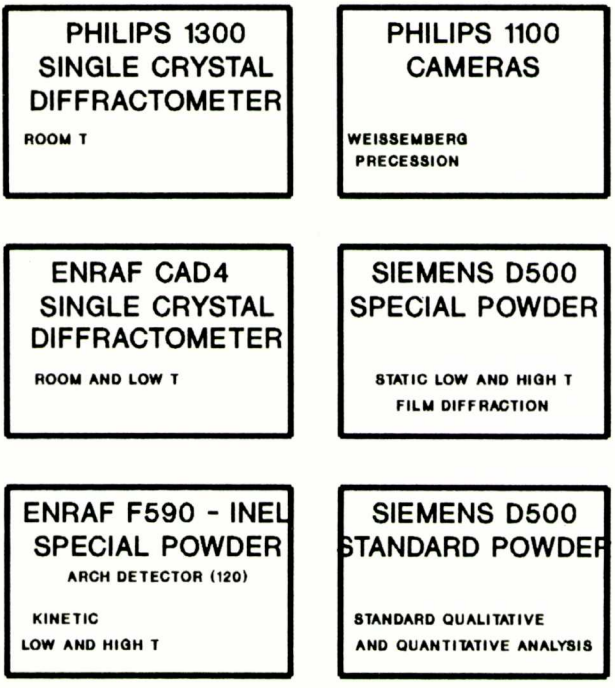

Fig. 3. The schema fo X-ray diffraction equipment at the University of Barcelona.

ternal symmetry of series of crystals to deduce variation in habitus as opposed to temperature in some industrial crystals (pictorial materials).

Optical crystallography was another technique used to find out the optical properties of new crystals, like optical ellipsoid, optical indexes (α, β, γ), position of the axes of the ellipsoid related to crystallographic symmetry, and general optical conditions such as color, transparency, etc. (Fig.4 and 5). The Department has a number of polarizing microscopes for student use, and substantial range of optical equipment of photosensitive systems for light between 250 nm to 1100 nm, with a system of quartz objectives and diaphragms that do not stop ultraviolet or infrared light. This equipment is connected to a microelectronic system to produce an automatic management of the scanning stage and provides the facility to calculate the optical density of light statishcally, in transmission and reflection. Some research papers on properties of adsorbing crystals, and the claculation of n and k, have been published (fig. 6).

The structural crystallographic research unit is formed at present by two specific groups:

Fig. 4. Cobalt ethylenediaminetetraacetate (CoEDTA) crystal. (From PhD of M. Font-Bardia at the University of Barcelona).

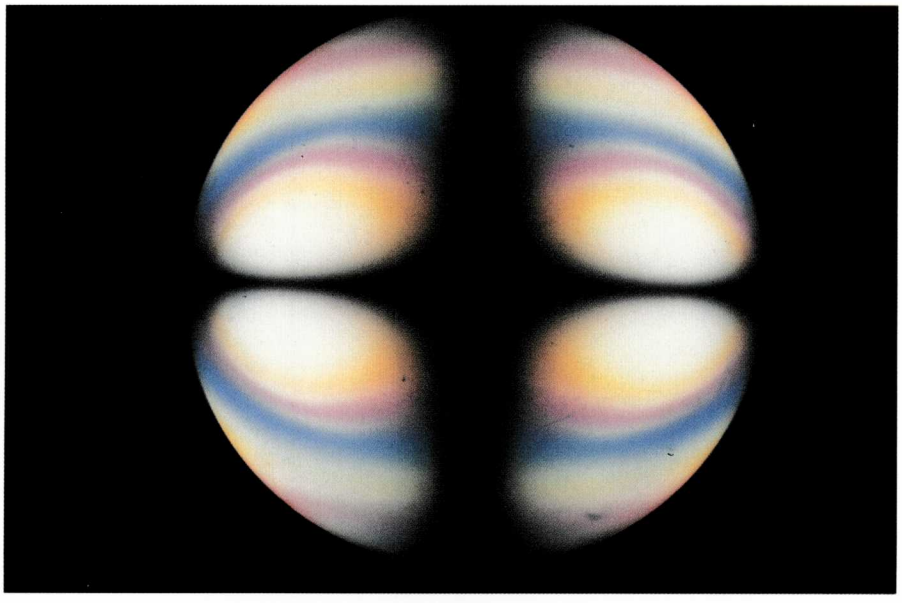

Fig. 5. Biaxic interference figure seeing two optical axes.

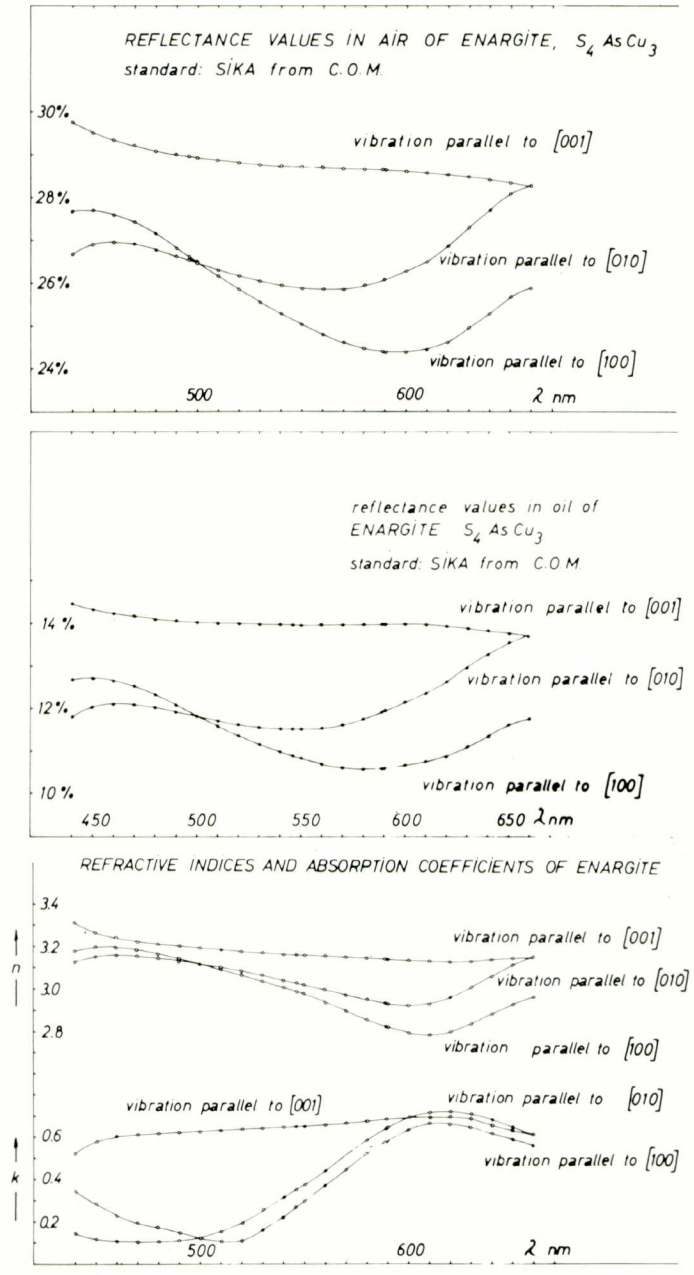

Fig. 6. Reflectance values in air, Ra, and oil, Ro, with the calculated n (refractive indeces) and k (absorption coefficients) of enargite, S_4AsCu_3. (From M. Vendrell, A. Lopez-Soler and J. M. Bosch-Figueroa).

a) One, directed by professor Salvador Galí, carries out research on growing crystals in the solid state (essentially hexaferrites), and the structural analysis of some of them. In the majority of cases, the crystals are so small that it is necessary to use the powder diffraction method to obtain X-ray information. The crystal structure of the samples is known, so the Rietweld method is used to obtain more accurate information on the distribution of specific atoms by blocks. This group has a series of furnaces with temperatures up to 1600°, in normal or controlled atmospheres, with special electronic and mechanical systems that can be applied to the furnace to grow crystals in specific conditions. They have published about 30 research papers, in Afinidad, Anales de Química, Journal of Applied Crystallography, Material Research Bulletin, N. Jb Miner. Mh., etc.

b) The other, directed by professor Xavier Solans, carried out research work on crystal and molecular strucure analysis of samples coming form different laboratories of the University of Barcelona or from other Spanish Universities such as Oviedo, Bilbao, Zaragoza, Valencia, Murcia, Badajoz, Granada, etc. The research of this group has different connections with foreigh Departments such as the Institute of Crystallography of Moscow and the Department of Fine Organic Synthesis of Sverdlovsk (Urals Division) of the USSR Academy of Sciences, through the Institut d'Estudis Catalans; the Laboratoire electrochimique des Métaus de Transition of the Orsay University (Paris); the Laboratoire de la Chimie de Coordination of the Paul Sabatier University (Toulouse); the Department of Inorganic Chemistry of the Autonomous National University (Mexico) and the Guanajuato National University of Mexico; and the Chemistry Department of the National University of Bogotá. Fig. 7 and 8 show the schema of the general hardware and software used for the solution and refinement of the structure of crystals. As an example of the work of this group the drawing solutions (ortep and moldraw) of the 6,7-dimethyl-2,3-bys (2-pyridyl) quinosaline-hexafluoroacetylacetonatecobalt (II) (Co (DMeDPQ) $(hfacac)_2$) are shown in figures 9 and 10.

We wish to emphasize the main problems in crystal structure determination: the quality of crystals and the purpose of determination. The working methods differ according to the purpose of crystal structure determination, high accuracy implies a higher number of reflections observed, or a higher time in the diffractometer to the detriment of the number of crystal structures determined in a year. Poor crystal quality produces a lower number of reflections observed which influences in solution obtained. A short study of the influence of the número of reflections observed in the different stages of analysis, which are shown in fig. 11 to 14, is explained in the next section.

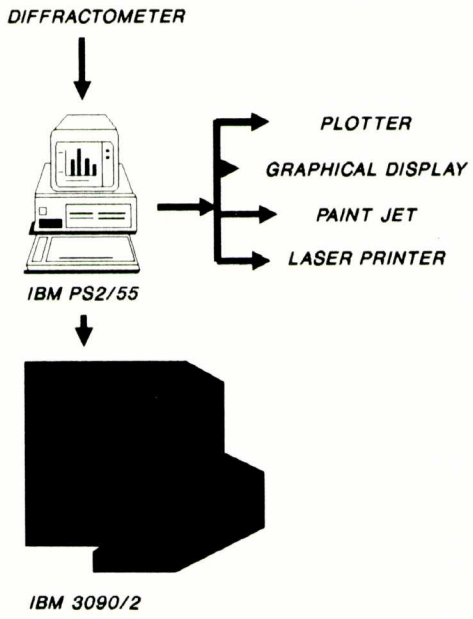

Fig. 7. The schema of the hardware crystal structure determination.

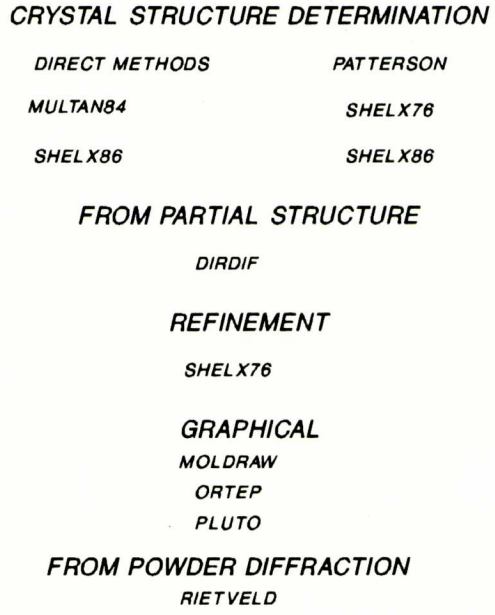

Fig. 8. The schema of the software crystal structure.

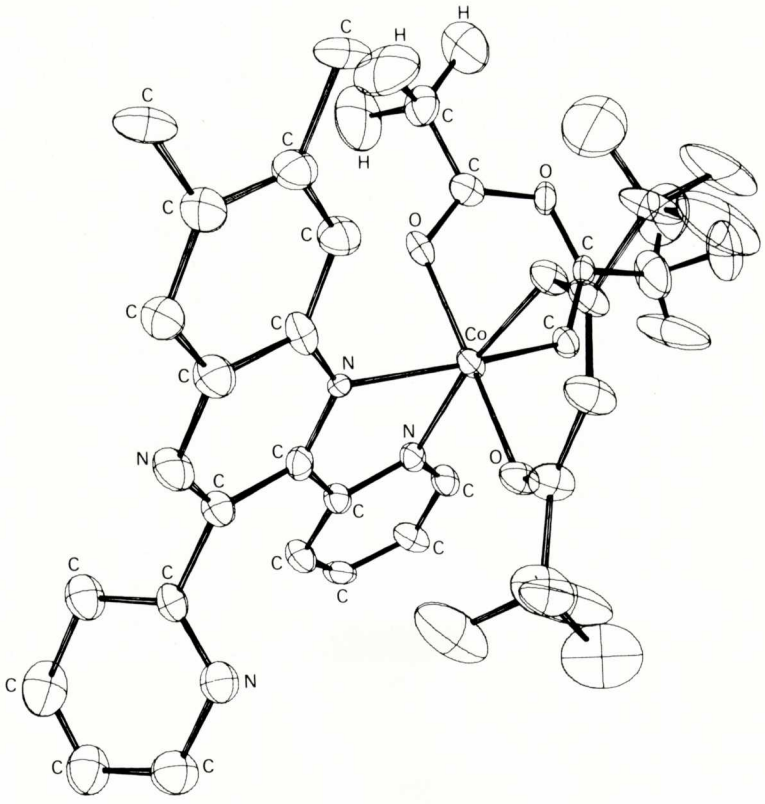

Fig. 9. Drawing solution of the 6,7-dimethyl-2, 3-bys (2-pyridyl) quinosaline hexafluoroacetylacetonate cobalt (II) ($C_{30}H_{20}N_4O_4F_6Co$) molecule with ORTEP program. (From A. Escuer, R. Vicente, T. Comas, J. Ribas, M. Gómez, X. Solans, D. Gattesh and C. Zanchini; Inorganic Chimica Acta 181 (1991) 51-60).

A) *Multan 84.* The number of reflections used in the Multan program is independent of the number of reflections introduced, because it is defined by the number of non-hydrogen atoms in the unit-cell, the space group and the value of normalized structure factor, but all the reflections introduced are used determine the Wilson plot, poorer result being produced as fewer reflections are introduced. This alters the normalization of sturcture factors, convergence mapping and the best phase set, and as a result the solution.

B) *Shelx 86 (direct methods).* The number of reflections used in refinement and the number of non-negative quartets are bounded by the program, as the fewer the reflections introduced in the program, as the higher

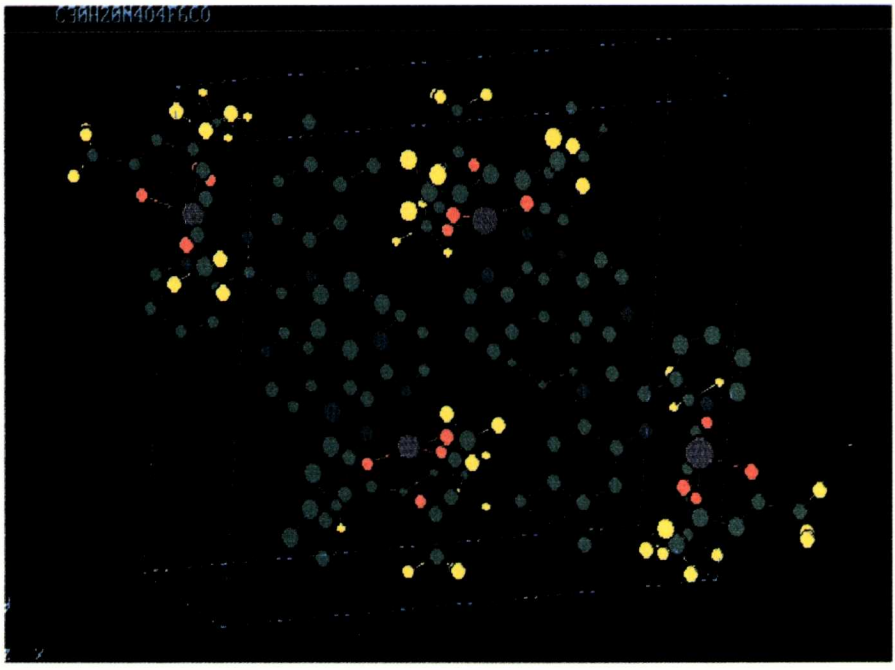

Fig. 10. Drawing solution of the 6,7-dimethyl-2, 3-bys (2-pyridyl) quinosaline hexafluoroacetylacetonate cobalt (II) ($C_{30}H_{20}N_4O_4F_6Co$) unit cell structure by means of MOLDRAW program. (From A. Escuer, R. Vicente, T. Comas, J. Ribas, M. Gómez, X. Solans, D. Gatteshi and C. Zanchini; Inorganic Chimica Acta 181 (1991) 51-60).

the number of non-negative quartets obtained, and the structure is not determined.

C) *Patterson.* No incluence of the number of reflections introduced can be observed.

D) *Refinement.* The influence in refinement is doubled, it alters the speed of refinement and the accuracy. The velocity can be observed from the equation defining the computed structure factor, a higher slope being observed for contributions of heavy atoms or reflections of a high order, so, differences between F_0 and F_c show less dispersion of refined parameters if they correspond to heavy atoms or if reflections of a higher order are used. As the values of first and second derivatives depend on the old parameters, the refinement shows minimum wavering when reflections with higher Miller indexes are used. The influence of the accuracy of results is shown in the adjoining schema, and as a higher number of reflec-

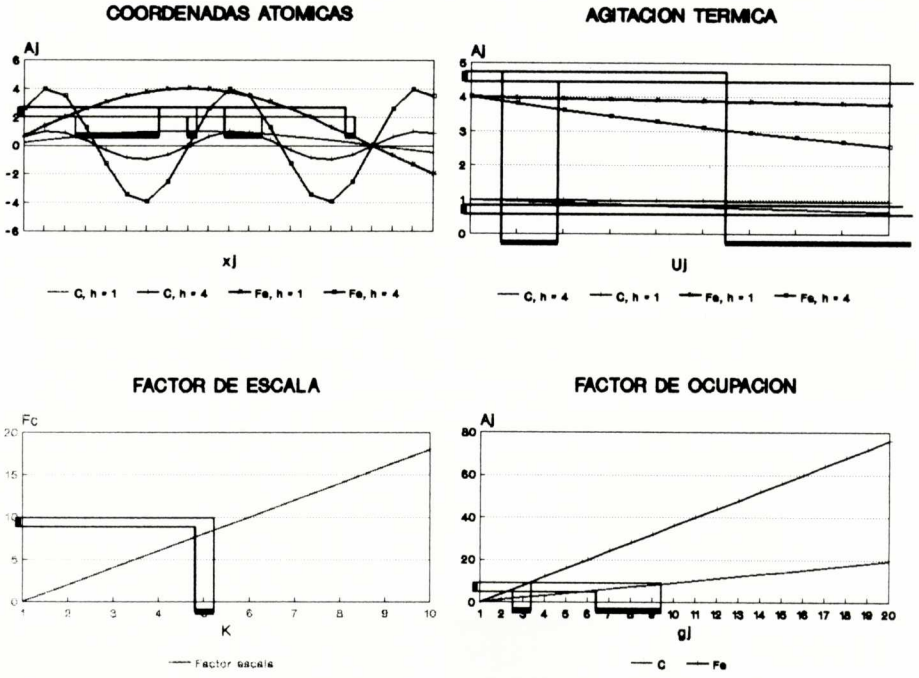

Fig. 11. Influence of the number of observed reflections in refinement the speed
$$Fc = K\ Aj$$
$$Aj = fj\ gj \exp(2ihxj) \exp(-hUjh)$$

tions is used, we obtain fewer standard deviations, less dispersion in equivalent bond lenght and angles, although the R index increase (in spite of the fact the R-index tends to diminish when better is the structure)..

E) *The quality of crystal.* A random error has been introduced into the values of structure factors observed, increasing a percentage of their value randomly plus or minus. The results are obvious: increasing the error, means an increase in the R value and dispersion between equivalent bond lengths.

Our group is carying out the determination of the atomic structure of magnetic crystals, previously studied as regards their magnetic properties in the Faculty of Physics, in order to obtain information on the effects of directions of strong bonding, and also, through powder diffraction at different temperatures, the possibl changes appearing. In addition, we are now studying differences in structure transition produced by low temperature effects to obtain the best data for bonds and angles of special structure crystals.

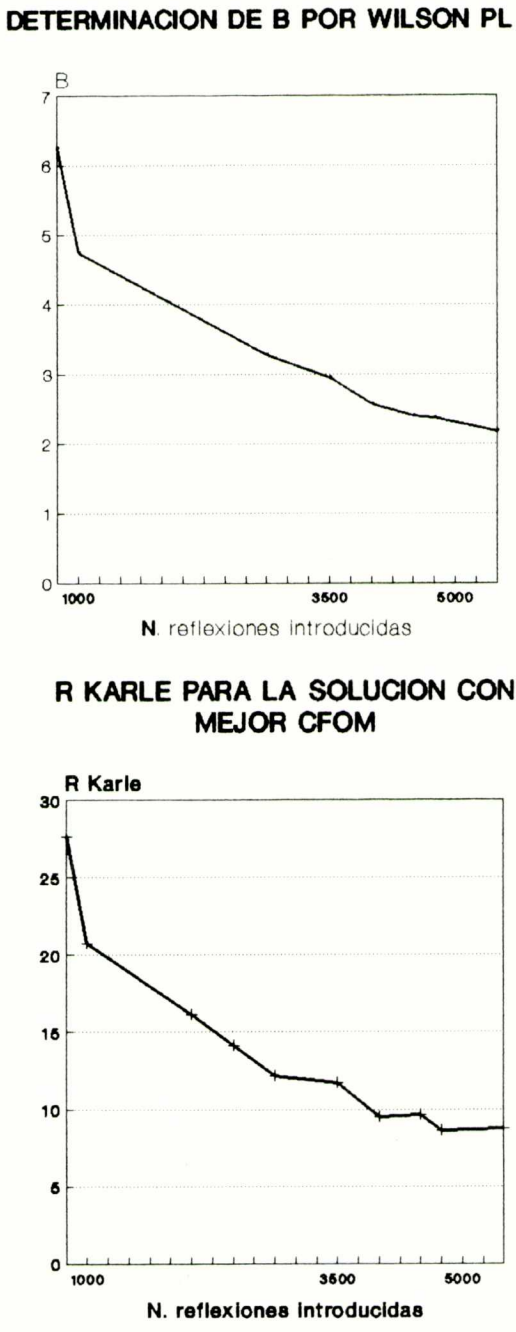

Fig. 12. Influence of the number of observed reflections in MULTAN84.

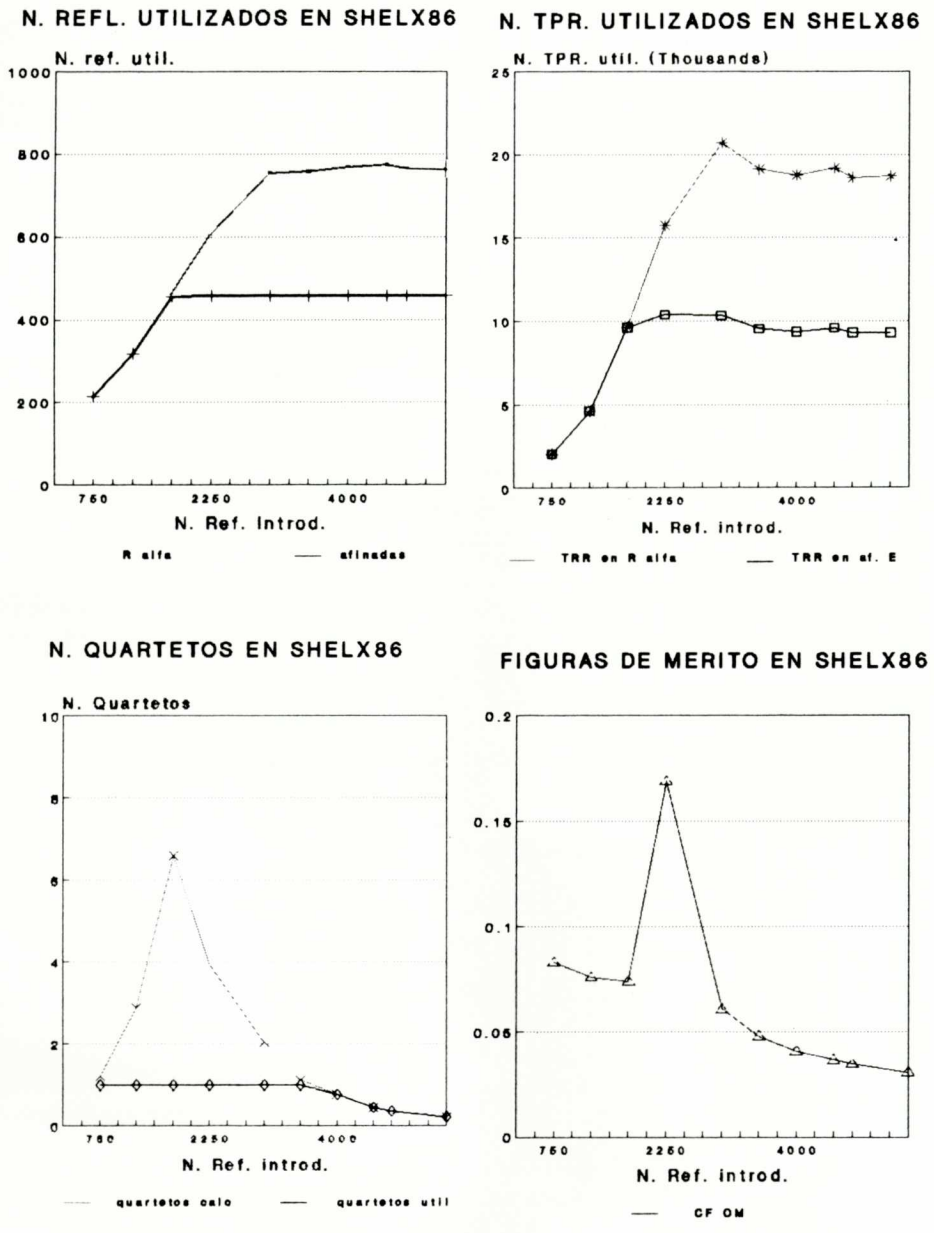

Fig. 13. Influence of the number of obsewrved reflections in SHELX86.

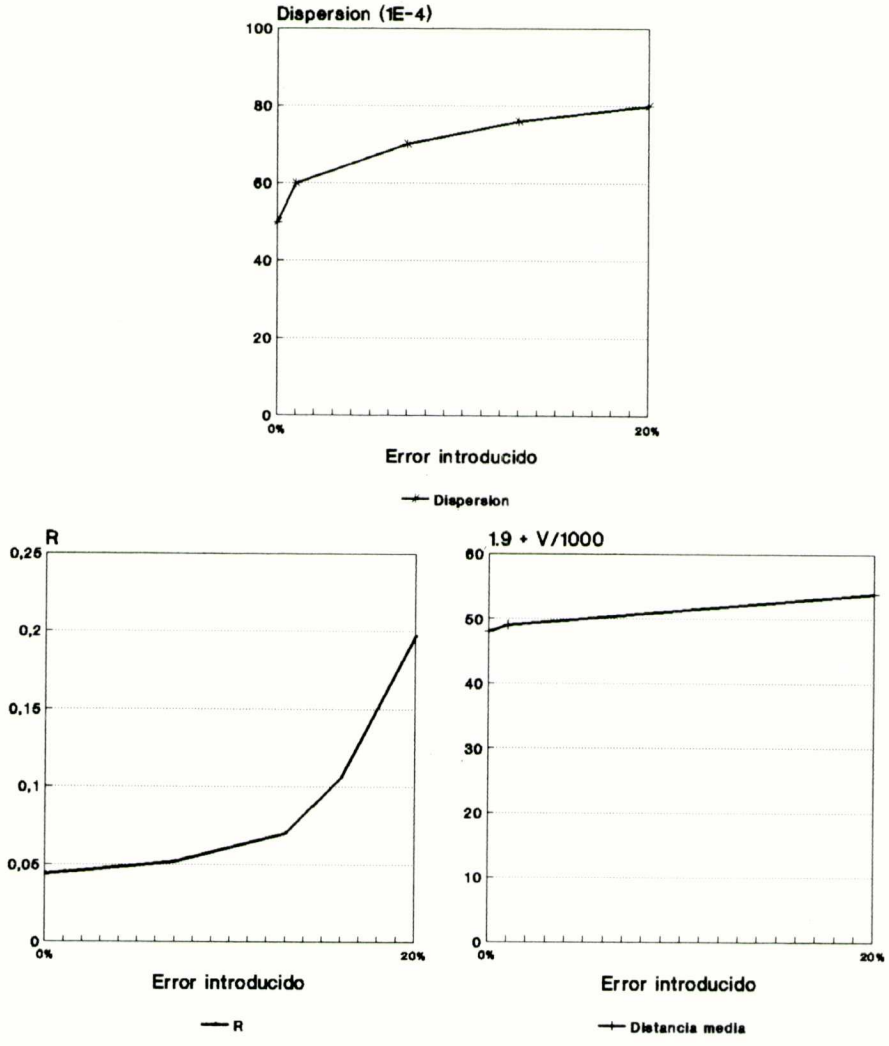

Fig. 14. Influence of measurement errors in the refinement.

The group have published nearly 250 papers in journals such as Acta Crystallographica, Inorganic Chimica Acta, Inorganic Chemistry, International Journal of Peptids and Protein Research, Journal of Applied Crystallography, Journal of Biomolecular Structure and Dynamics, Journal of Chemical Research, Journal of Chemical Society (Chemical Communications and Dalton Transactions), Journal of Crystallographic and Spectrocopic Research, Journal of Organometallic Chemistry, Organo-

metallics, Polyhedron, Powder Diffraction, Tetrahedron, Transition Metal Chemistry, Zeitschrift für Kristallographie, Afinidad, Acta Geologica Hispànica, etc.

In normal circumstances, taking in account the availability of new equipment and the damage to old pieces, and also the quality of crystals received for their structure to be solved, only about 50% of crystals having a sufficiently high quality for X-ray diffraction, the structural crystallographic group are able to evaluate between 60 and 80 structures per year, at present.

The Scientific Technical Services of the University of Barcelona has a Powder X-ray Diffraction group for the general services of the University and for services to Industry. The equipment of the group consist of three diffractometers on powder samples, two Siemens D500 and one Enraft with an inel detector. One of the Siemens works with standard samples gi-

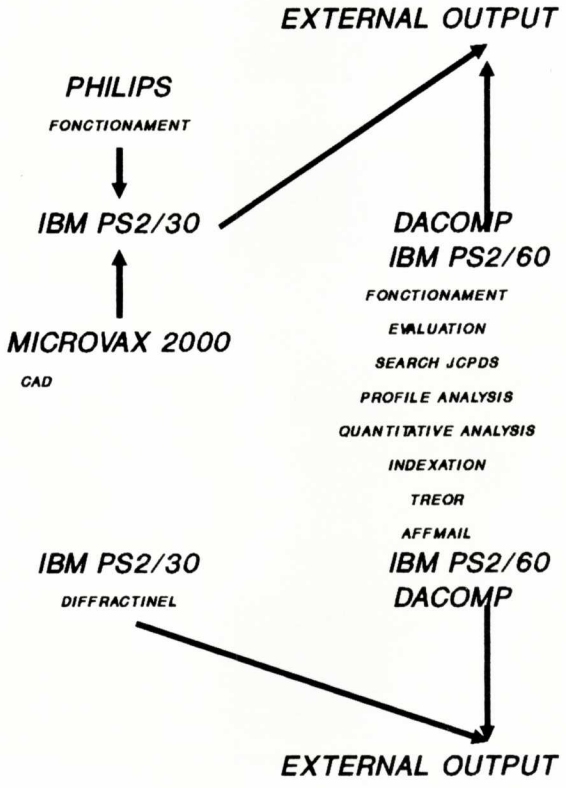

Fig. 15. The schema of the software used to solve the powder diffraction data.

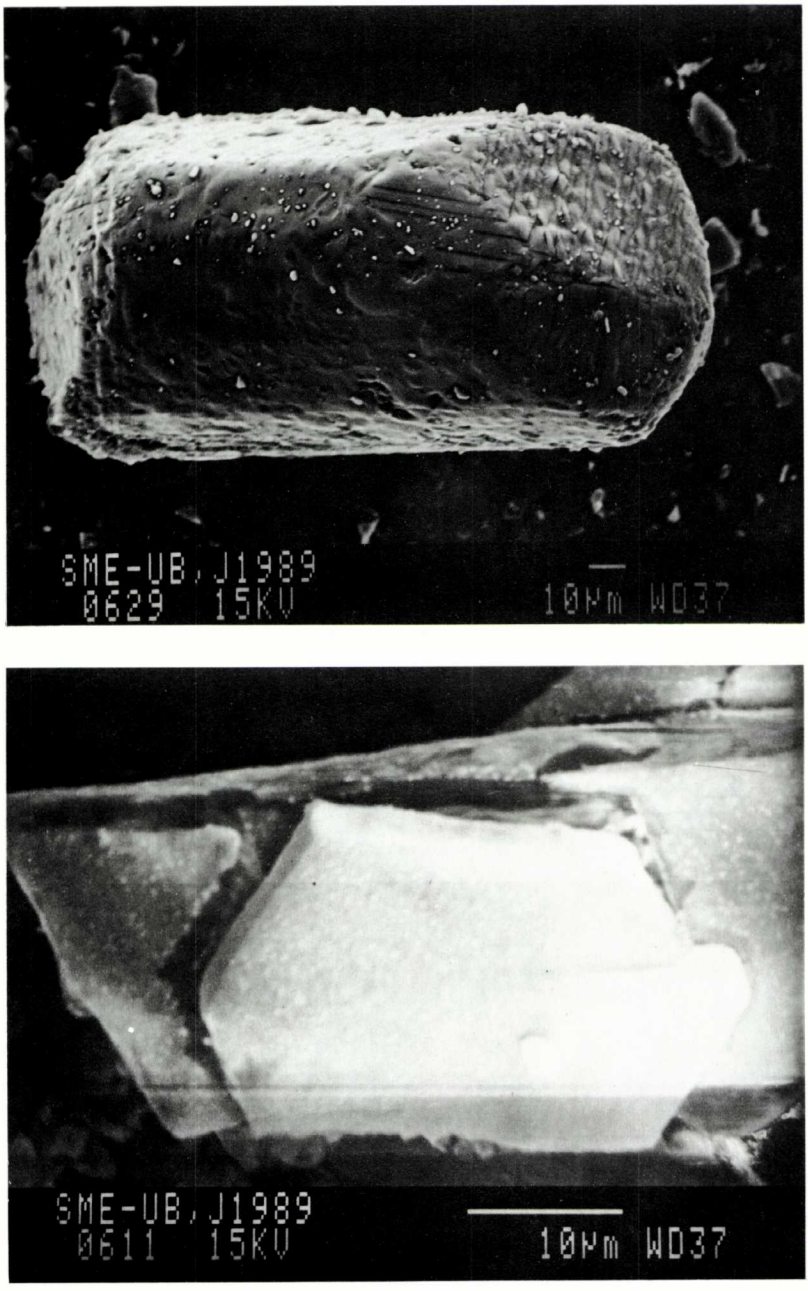

Fig. 16. Electron microscope photograph of two EDTA derivate crystals.

ving results to users to identify materials and to provide the standard spectrum of new compounds; the other Siemens has low and high temperature accessories and is normally used by the molecular alloys and isomorphism group of the Department; both Siemens diffractometers are arranged to work in equilibrium in order to attend all possible users. The Enraft-Intel diffractometer has an arch detector of 120° and its service is essentially for kinetic processes; the speed in obtaining the spectrum is fast, between 3 and 15 minutes, and the accuracy of the position and intensity of peaks is good. Every piece of equipment is ruled by a microcomputer, which is connected to a personal computer in order to be able to obtain and work with data (the schema is shown in fig. 15). All software on powder diffraction (Siemens special software) is operated with one PS2/30 and two PS2/60 IBM computers.

Electron microscopy, both of the transmission and scanning type, is a form of a technical assistance used to study the form of microcrystals, the microanalysis and the map distribution of elements in very small crystals. In fig. 16 two crystals of ethylenediaminetetraacetate derivates are represented, and in fig. 17 a mapping of the elements in a sample of pictorial

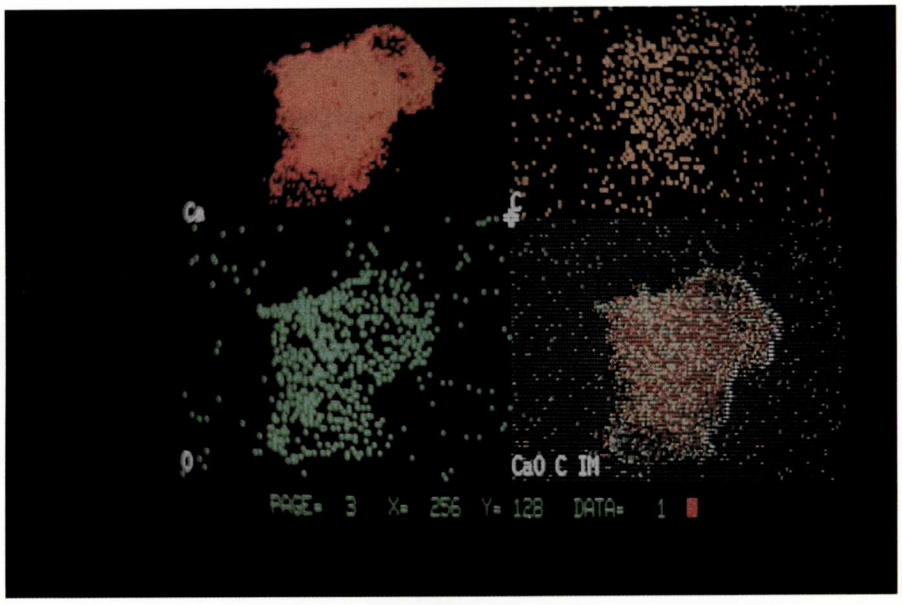

Fig. 17. Mapping of the elements in a sample of pictorial material with their superimposition so as to provide a combination of them.

material with their superimposition so as to provide a combination of them. The colors of the mapping are not real colors, the photograph has 256 different types of white, grey and black, but every one of there greys is associated with one series of imaginary colors given to the drawings that can be seen.

The electron scanning microscope with microanalysis by EDX is absolutely necessary to study the pictorial materials of wall paintings of 11th, 12th and 13th centuries, thoses on wood of 15th century, and in general to do any research work of this type on oil paintings.

Abstract

In the area of Barcelona there exists at present four important Centers where different types of X-ray diffraction are carried out. In the University of Barcelona X-ray diffraction is in existence in two Departments: the Crystallography, Mineralogy and Mineral Deposits, and the Scientific Technical Services.

The first is a complex center in the Faculty of Geology created in 1912 as a group to study minerals and general mineralogy; crystallography was necessary to understand mineralogical properties and, in the course of time and as a result of personal efforts, it has become one of the most important parts of the group. Goniometry started in the twenties with the study of the geometrical forms of crystals and, thereafter, their symmetry. In the thirties X-ray diffraction in single crystals was developed with some special studies published in Zeitschift für Kristallographie. Our Civil War stopped this research for several years and the isolation of our country during the World War and the forties and fifties prevented us from having high-level contacts with world crystallographic science. We wish to recall the difficult tiems overcome by the effort of Professors F. Pardillo and J. L. Amorós, who worked in Barcelona on crystallography and who were know in the world of our science. Today, the Department is a center with a high level of scientific work.

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A detailed description of X-ray diffraction in both Departments are explained, with some possible solutions to the problems arising from the developing of the analysis of crystal structures.

REFERENCES

The crystallographic research papers of the Department of Crystallography, Mineralogy and Mineral Diposits have been published in the standard journals of this field mentioned in the present text.