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Fifty years of Rietveld refinement: Methodology and guidelines in superconductors and functional magnetic nanoadsorbents

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Abstract
A proper initiation into the Rietveld refinement method can be slow, taking into account the accelerated rhythm of the research and economic demands. Therefore, this work fills this gap, providing the basic foundations and methodology of the Rietveld refinement. Also, it exposes the results of its application in superconducting samples of yttrium barium copper oxide, magnesium diboride, and functional magnetic nanoadsorbents of maghemite and a multiphasic composite (iron oxide, hydroxyapatite, and secondary phases). In the process, an in-detail protocol was designed and provided, with which all the studied samples got successfully refined. Thus, this work represents a quick introduction to the Rietveld method, for which beginners can obtain good results while making correct interpretations of the whole refinement process.

Keywords: superconductors, magnetic nanoadsorbents, Rietveld method, multiphasic analysis, microstructural parameters.

Cincuenta años del refinamiento Rietveld: Metodología y guía de uso en materiales superconductores y nanoadsorbentes magnéticos funcionales

Resumen
Una adecuada iniciación en el método de Rietveld puede ser lenta, teniendo en cuenta el ritmo acelerado de la investigación y las demandas económicas. Así, este trabajo cubre este vacío, proporcionando los fundamentos básicos y la metodología del refinamiento Rietveld. Además, expone los resultados de su aplicación en muestras superconductoras de óxido de itrio bario cobre y diboruro de magnesio, así como en nanoadsorbentes funcionales magnéticos de maghemita y un compuesto multifásico (óxido de hierro, hidroxiapatita y fases secundarias). En el proceso se diseñó y proporcionó un protocolo detallado, con el cual las muestras fueron refinadas con éxito Así, este trabajo representa una rápida introducción al método de Rietveld por el cual los usuarios principiantes pueden obtener buenos resultados mientras hacen interpretaciones correctas de todo el proceso de refinamiento.

Palabras clave: superconductores, nanoadsorbentes magnéticos, método de Rietveld, análisis multifásico, parámetros microestructurales.

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Introduction

Since its first application in 1975 on X-ray diffraction (XRD) pattern analysis [1], the Rietveld refinement method has been gaining popularity until today. It has been helpful in many crystallographic issues. One of the main contributions of this method is that the powder diffraction method stopped being only a qualitative method and was revitalized along with the Rietveld refinement into a whole quantitative phase analysis method [1, 2]. Moreover, its most relevant applications are the study of magnetic structures (neutron diffraction), phase quantitative analysis, texture analysis, structure determinations, and many others [3, 4].

These days, the Rietveld refinement method is an indispensable part of several crystallographic studies with synchrotron, powder, or neutron diffraction analysis. It works fine even when the analyzed structure is a complex one in terms of overlapping peaks [3] such as multiphasic composites. On the other hand, oxide functional materials and superconductors have been researched a lot lately because of their applications in many fields, such as in nanotechnology [5], environmental remediation [6], and renewable energy [7].

This work commemorates the 50 years since the inception of the Rietveld refinement method and recognizes its application in functional materials. Here, a practical guideline of the Rietveld refinement method and the refinement and analysis of precursors and superconducting samples got provided. These samples are copper oxide (CuO), yttrium oxide (Y_2O_3), barium carbonate ($BaCO_3$), $YBa_2Cu_3O_7$ (YBCO), magnesium diboride (MgB_2), and functional magnetic nano adsorbents (a multiphasic sample (MPS) and a bare nano maghemite sample (γ-Fe_2O_3), one of the MPS phases). It got also presented the in-detail analysis and comparison of these last two samples that have shown remarkable applications in environmental remediation and healthcare [6, 8]. In this way, their microstructural parameters: crystallite size, and lattice strain, are obtained. As a byproduct of this work, a detailed refinement protocol got designed and applied with FULLPROF Suite because of its free availability and friendly platform.

The Rietveld Refinement Method

In the words of George Will, "the Rietveld refinement method is a least-squares refinement procedure where the experimental step-scanned values are adapted to calculated ones" [3]. In other words, the Rietveld method starts comparing an experimental diffractogram with a theoretical model. Then, it uses the least-squares method in software such as FULLPROF Suite, TOPAS, and GSAS (in this work, the former got applied in all the presented refinements). Hence, it minimizes the difference between the intensities of the calculated diffraction profile (y_{calc}) and the observed ones (y_i) [9]. This difference is gotten by the least-squares function as follows:

$$S_y = \sum_i w_i (y_i - y_{cal})^2 \tag{1}$$

where $w_i = 1/y_i$ is the weight. This method leads us to find optimal values for some parameters (which will be defined later) that allow S_y to be the smallest possible. Moreover, since diffractograms come from monophasic or multiphasic samples, two approaches are distinguished: monophasic samples refinement and MPS refinement.

Monophasic Samples Refinement

In monophasic samples treatment, the parameters that contribute to the intensities y_{calc} of each point of the model can be expressed by:

$$y_{cal} = s \sum_K m_K L_{pK} |F_K|^2 \phi(2\theta_i - 2\theta_k) P_K A + y_{bi} \tag{2}$$

where K represents the Miller indices (hkl) and the factors in eq. 2 are the following:

Scale Factor (s)

s is an arbitrary factor that normalizes the calculated intensity concerning the observed ones. Therefore, the intensities of the peaks will be proportional to s [9, 10].

Multiplicity Factor (m_K)

In powder XRD, there are some reflection angles in which more than one reflective plane contributes. In these cases, the measured intensity is the sum of each contribution. The number of these contributions is called reflection multiplicity. Thus, the multiplicity factor is a function of lattice symmetry and its reflection planes [9, 11].

Lorentz-Polarization Factor (L_{pK})

It contains the geometrical features of the XRD experiment, such as the reciprocal lattice configuration of the sample and the slit length of the diffractometer [9, 12].

Structure Factor (F_K)

It is expressed as:

$$F_K = \sum_j N_j f_j \exp 2\pi i(hx_j + ky_j + lz_j) \exp -M_j \tag{3}$$

where j refers to the unit cell atoms, N_j is the site occupancy divided by the site multiplicity, f_j is the atomic form factor, h, k and l are the Miller indexes, x_j, y_j and z_j are the atomic positions and Mj contains the thermal contributions (atomic displacements) [10]. It is suggested to take a look at a Solid State Physics or XRD book for a major understanding of this factor [10,12].

Reflection Profile Function (ϕ)

It includes the effects of instrumental features, transparency, specimen displacement, crystallite size, and microstrain, and also it gives the shape to the diffraction peaks as will be shown later [10].

Preferred orientation (P_K)

One of the advantages of powder XRD is to obtain uniform statistic distributions in crystallite orientations. This factor describes the lack of randomness in these orientations. Its contribution can be decreased by correctly pulverizing the sample.

Absorption Factor (A)

The absorption factor is related to the geometry and properties of the sample and experimental configurations [9].

Background (y_{bi})

The background is the incident noise that emerges from the instrument or the sample. Depending on its contribution, one chooses a background configuration or another one in FULLPROF Suite, as explained later.

Peak Shape profile and broadening

Many functions can accurately describe the shape of the peaks, such as Gaussian, Lorentzian, Pseudo-Voigt, Thompson-Cox-Hastings Pseudo-Voigt function (TCH), and Pearson VII [3,9].

In this work, the TCH function got used given that it describes well most of the diffractograms. Also, it easily allows users to obtain the microstructure parameters of the refined samples.

The peaks broadening is usually and successfully described by the Cagliotti parameters U, V, and W by the expression:

$$(FWHM)^2 = Utg^2\theta + Vtg\theta + W \tag{4}$$

where θ represents the diffractogram angles.

Until now, the most basic and mandatory equations and definitions got presented below the assumption that the reader has basic notions of X-ray diffraction theory, crystal structure, and powder XRD. From now on, taking into account the physics behind XRD and the Rietveld method for monophasic samples, the necessary practical knowledge is provided.

Monophasic Samples Refinement Guidelines

Before every refinement, the XRD data corresponding to the crystallographic phase must be identified and indexed with a reference sample available in the literature using MATCH v3 software, for example. This reference (Powder Diffraction File-PDF 3 or 4) will work as an initial model from which the refinement will start. Another requirement is to know the instrument, diffraction type, sample treatment, and preparation/synthesis information (sample's history). Once all these requirements are accomplished, the first step in the Rietveld refinement is to introduce this information in FULLPROF Suite (or any other program in use) along with the configurations one prefers, such as the peak shape function, geometry function, or the background configuration. Then, iterations can begin. But, before each one, the parameters to refine must be chosen while taking into account the results you are getting after each refinement and their physical meaning. In order to understand this, in the following subsection, the general meaning and practical information of each refinement parameter are given.

Refinement Parameters

- Scale factor: As mentioned before, this factor will normalize the calculated diffractogram concerning the observed one. Thus, by refining it, any disproportion between these diffractograms will be erased. It usually is refined along with the other parameters as a streamline for iterations.

- Background parameters: There are two common ways to configure this set of parameters. The first one is by defining a polynomial function, where the refinement parameters would be its coefficients. In this configuration, the background parameters are between the first ones to be refined until one gets a calculated background line that matches with the observed one.

  The other configuration is by interpolation with a set of background points. These points get chosen by the user in WinPLOTR. Therefore, it allows having a more accurately background line. However, it is suggested to refine these points at the end of the whole process to avoid unnecessary underestimations of the peaks.

  The approach in most of this work is to use both configurations, starting with a polynomial function background. And then, once the refinement gets almost done, this background configuration is changed to another one to eliminate the irregular noises [13,14].

- Instrumental parameters: In most cases, the only instrumental parameters that one needs to refine are the zero detector and the displacement. These two can adjust the calculated pattern angular positions as a whole to the observed one. The thickness of the sample is attributed to be infinite in some models. However, when the atoms are too light, transparency refinement should be considered along with the geometry models [9, 14]. In this work, Bragg-Brentano geometry got used.

- Lattice parameters: The refinement of these parameters fits the Bragg positions of the model. And since it contributes powerfully to this, its high variation could be very risky. Fortunately, if the initial model got chosen correctly, these parameters should not change too much.

- Profile parameters: Shape, asymmetry, and Cagliotti parameters define the broadening and shape of the peaks. They are a lot sensitive, and many errors arise while refining them. It is suggested to consult these issues with a wider guideline [14]. However, some advice about it is given later.

- Atomic parameters: These parameters will contribute directly to the intensities of the peaks. However, one must be careful when refining them because physical incongruities can arise from them. For instance, thermal factors represent the vibration intensities of the atoms in the unit cell. Thus, its negative value would not make physical sense at all. A change in the occupancy could induce a disproportion in the number of atoms of an element in unit cells. And also, atomic position variations could disturb the whole model. For these reasons, refining these parameters as one of the last steps would be wise.

Multiphasic Samples Refinement

The intensity function for MPS is the sum of the intensity of each phase. Thus, the intensity expression is expressed as follows [15]:

$$y_{cal} = \sum_{P} s_P \sum_{K} m_K L_{pK} |F_K|^2 \phi(2\theta_i - 2\theta_k) P_K A + y_{bi} \tag{5}$$

where the clear difference with eq.2 is the new sum term, $\sum_P s_P$, and it represents the overlapping of each phase contribution to the total intensity. In the refinement of these samples, one must constantly remember that each phase contributes individually. Thus, at first, the difference in intensities could point out that other phases are still unrefined.

Statistical Parameters

The quality of the refinement can be checked out in each iteration by the Rietveld R-factors R_p, R_{wp}, R_{exp}, and χ^2 [13]. The χ^2 is defined by:

$$\chi^2 = R_{wp}/R_{exp} \tag{6}$$

In general, the refinement's goodness can be verified by satisfying that the χ^2 factor is as small as possible. The χ^2 should be understood as an indication of that the employed theoretical model matches correctly with the experimental one. If, after an iteration, it arises or decreases, the model becomes worse or better, respectively. Also, if this parameter is less than one, the R_{exp} could be too high, or the data quality too low [9, 13, 14].

However, sometimes to consult this factor won't be enough. One can find a situation in which the peaks won't fit well even with a low χ^2 value. Therefore, one must be aware of both the visual pattern and these statistical indicators, all of this paying attention to any non-sense in the physical meaning of refinement parameters [9, 14].

Materials and Methods

Diffraction data of CuO, Y_2O_3, $BaCO_3$ and YBCO was acquired from a Siemens D5000 diffractometer operating with 2θ = 10-80° (8-80° for YBCO sample) step scanning mode, a 0.02° step and a 1 s/step resolution. The standard used in the refinement of these samples was SiO_2. Meanwhile, MgB_2, γ-Fe_2O_3 and MPS diffraction data was obtained from a Rigaku diffractometer, operating with 2θ=8-80° step scanning mode, a 0.01° step and 1 s/step resolution. In this case, the standard was Al_2O_3. Both diffractometers applied CuK$_\alpha$ radiation (1.5406 Å).

PCR Editor and WinPLOTR, two of the available tools in FULLPROF Suite, were used in the refinements because of their free-of-charge distribution. In WinPLOTR, sets of background points were made in BGR files and introduced in the corresponding PCR files. Match v.3 was used for the samples identification in order to collect the initial models for the refinements of each sample in CIF with the following identification codes: #7212242 (CuO), #9006317 (γ-Fe_2O_3), #1009013 (Y_2O_3), #9013804 ($BaCO_3$), #1008353 ($YBa_2Cu_3O_7$), #1000026 (MgB_2) and for the MPS: #1517238 ($Ca_3O_8P_2$), #9012692 (Fe_2O_3), #9002213 ($Ca_5HO_{13}P_3$), #9014772 ($CaCO_3$), and #9007619 ($Ca_4H_4O_{16}P_4$). The diffractogram figures and 3D electronic density maps were made in OriginPro 9.0, and the atomic structures were designed in VESTA free software. To obtain the crystallite size and strain of each sample, the Instrumental Resolution Function (IRF) file of each standard was generated and inserted in the PCR files.

Refinement Protocol

As a byproduct of this work, a Rietveld refinement protocol was designed, presented, and partially used in the samples refinement. The following set of steps represent the designed refinement protocol.

1. To collect experimental and sample information.

   As mentioned before, the user must have in mind the sample preparation and history for the sake of reducing errors in optical diffraction conditions (zero detector, transparency, displacement, or wavelength) and other physical incongruities.

2. To get a suitable Crystallographic Information Framework (CIF) using MATCH, QualX, or any other software.

   It is important to choose a CIF that doesn't differ too much from the experimental data because it will ease the whole refinement.

3. To insert the required information in the program, from the CIF file and the available information of the diffraction experiment.

   It is recommended to use initial FWHM parameters close to U=0.03, V=-0.03, and W=0.03 for nanoscopic samples. These values have been chosen because they have given a well approximated broadening for nanoscopic samples peaks. Otherwise, other values can be chosen as in the case of bulk samples, in which the broadening of the peaks are thinner so the Cagliotti parameters could have shorter absolute values. For instance, U=0.003, V=-0.003, and W=0.003.

4. To refine the scale factor.

   One must be aware of the underestimation of the scale factor. Sometimes, one could get a flat model because the refinement of this parameter decreases too much. In those cases, it is suggested to refine one cycle at a time until the model peaks are near to the experimental peaks level. One can type it too, or both.

5. To refine the scale factor and zero parameters.

6. To refine the background parameters.

   When one has chosen a polynomial function background model, the refinement of these parameters should be done, at first, one by one and in order. If one has chosen a set of background points by linear interpolation, then it is suggested to not refine them until the end of the protocol if necessary.

7. To refine the scale factor and zero parameters.

8. To refine the zero and cell parameters.

   At this point, one should compare the Bragg positions of the model and the positions of the experimental peaks. If they differ too much, to try using another CIF and start again is suggested. It could get considered later too.

9. To refine the scale factor and shape parameters.

10. To refine the scale factor, shape parameters, and V.

11. To refine the scale factor, shape parameters, and W.

12. To refine the scale factor, shape parameters, and U.

    It could be useful to consider the peak broadening formula (eq. 4). That way, one can notice the kind of variation in the calculated profile that Cagliotti parameters produce when one refine them.

13. To refine the scale factor, shape parameters, and I_G.

    Now one can refine two FWHM parameters at once trying different combinations and sometimes even three or all of them at once. One must take into account that U and W must be positive while V must be negative or very close to zero. If, after a refinement, this doesn't agree, a backup file should be used to avoid the previous result.

14. To refine the atomic positions.

    One must be aware of which atomic position parameter must be refined. Sometimes one could get an error window because of the refinement of forbidden parameters.

15. To repeat the refinement steps until now.

16. To refine the asymmetry parameters.

17. To refine the refinement steps until now.

18. To refine the thermal factors.

19. To refine occupancy parameters.

    Users must remember that, in order to narrow down parameters, one can use the Restraint option in the PCR editor's main window.

20. To refine the refinement steps until now.

Results and Discussions

X-Ray Diffraction analysis

Refined parameters of the precursors and superconducting samples got exhibited in Table 1 with their statistical parameters. Also, its refined diffractograms got shown in Figure 1. The green vertical lines are the Bragg reflection positions. The black circles represent the experimental data, the red line is the calculated pattern, and the blue line is their difference. One can observe that the refined diffractograms and their χ^2 factors are correlated. In the YBCO case, this value is close to one. It has a direct correlation with the R_{wp} and R_{exp} ratio (See eq. 6). This was also seen in Figure 1.

The MPS got refined as a combination of an iron oxide magnetic phase and others coming from hydroxyapatite derivatives and then compared with the γ-Fe_2O_3 sample. Their refinement and statistical parameters are shown in Table 2. Given the complexity of MPS refinement, the obtained χ^2 parameter is the highest in this work. However, 5.9 is still an acceptable value.

The crystallite size and lattice strain of each sample were obtained by the Rietveld refinement method (Table 3). Also, it was possible to determine the percentage of intensities contribution of each phase.

On the other hand, as evidenced in Figure 2, the γ-Fe_2O_3 phase contribution is barely noted near its main peak in $2\theta = 35.59°$. Thus, the contributions of the highest peaks got attributed to the other phases. It is in agreement with Table 3 where the γ-Fe_2O_3 contribution is reported as just 0.8%.

N	Sample	Atom	Position coordinates			Thermal parameter ($Å^2$)	Lattice parameter (Å)	Statistical parameter
			x	y	z			
1	CuO (Monoclinic System)	Cu1	0.2500	0.2500	0.2500	0.0000	a = 4.6867	$R_p = 14.5$
		O1	0.000	0.4160	0.2500	0.0000	b = 3.4237	$R_{wp} = 10.1$
							c = 5.1312	$R_{exp} = 7.97$
							$\alpha = \gamma = 90°$	$\chi^2 = 1.60$
							$\beta = 98.49°$	
2	$BaCO_3$ (Orthorhombic system)	Ba	0.2500	0.4164	0.7530	0.6076	a = 5.3118	$R_p = 12.2$
		C	0.2500	0.7664	-0.0823	1.0000	b = 8.9000	$R_{wp} = 15.7$
		O1	0.2500	0.9010	-0.1125	0.9992	c = 6.4310	$R_{exp} = 9.70$
		O2	0.4602	0.6802	-0.1065	1.0000	$\alpha = \beta = \gamma = 90°$	$\chi^2 = 2.61$
3	$YB_2Cu_3O_7$ (Orthorhombic system)	Ba	0.5000	0.5000	0.1832	0.0001	a = 3.8592	$R_p = 29.9$
		Y	0.5000	0.5000	0.5000	0.0688	b = 3.8844	$R_{wp} = 21.7$
		Cu1	0.0000	0.0000	0.0000	0.6408	c = 11.6668	$R_{exp} = 21.3$
		Cu2	0.0000	0.0000	0.3534	0.0033	$\alpha = \beta = \gamma = 90°$	$\chi^2=1.02$
		O1	0.0000	0.0000	0.1484	0.0001		
		O2	0.5000	0.0000	0.3956	1.0424		
		O3	0.0000	0.5000	0.3586	1.0279		
		O4	0.0000	0.5000	0.0000	3.1990		
4	Y_2O_3 (Cubic System)	Y1	0.9673	0.0000	0.2500	0.0000	a = b = c = 10.6020	$R_p = 9.91$
		Y2	0.2500	0.2500	0.2500	0.0000	$\alpha = \beta = \gamma = 90°$	$R_{wp} = 11.1$
		O1	0.3931	0.1540	0.3811	0.0703		$R_{exp} = 8.44$
								$\chi^2 = 1.74$
5	MgB_2 (Hexagonal System)						a=b=3.0853	$R_p = 147$
		Mg	0.0000	0.0000	0.0000	0.1605	c = 3.5235	$R_{wp} = 93.1$
		B	0.3333	0.6667	0.5000	0.1259	$\alpha = \beta = 90°$	$R_{exp} = 79.35$
							$\gamma = 120°$	$\chi^2 = 1.38$

Table 1: Rietveld refined parameters of the precursors and superconducting samples.

Phases		Atom	Position coordinates			Cagliotti Parameters	Statistical Parameters
			x	y	z		
γ-Fe_2O_3 (Triclinic System-monophasic sample-1)		Fe-oct	0.1250	0.8760	0.1260	U = 0.3740	$R_p = 35.0$
		Fe-oc2	0.8750	0.8750	0.8750	V = -0.7303	$R_{wp} = 35.0$
		Fe-tet	0.4990	0.4990	0.4990	W = 0.8125	$R_{exp} = 33.7$
		O1	0.1323	0.1278	0.6191	X = 0.0000	$\chi^2 = 1.08$
		O2	0.6385	0.6385	0.6385	Y = 0.2195	
Multiphasic sample-2	$Ca_3O_8P_2$ (Trigonal System)-2	Ca1	0.0000	0.0000	0.0000	U = 0.0897	
		Ca2	0.0000	0.0000	0.0132	V = -0.0163	
		P	0.0000	0.0000	0.0090	W = 0.0070	
		O1	0.0000	0.0000	0.0175	X = 0.1518	
		O2	-0.1591	0.1591	0.0136	Y = 0.0000	
	γ- Fe_2O_3 (Tetragonal System)-2	Fe1	2.4973	1.5790	1.4132	U = 0.0041	
		Fe2	0.9543	0.9543	0.0000	V = - 0.0076	
		Fe3	0.3640	0.8670	-0.0160	W = 0.0063	
		Fe4	0.1400	0.1400	0.0000	X = 0.0190	
		O1	0.6150	0.8690	-0.0140	Y = 0.0000	
		O2	0.1190	0.3770	-0.0050		
		O3	0.1370	0.8610	0.0070		
		O4	0.3830	0.6310	-0.0030		
	$Ca_5HO_{13}P_3$ (Trigonal System)-2	Ca1	0.6667	0.3333	0.0288	U = 0.0459	
		Ca2	0.2022	0.9796	0.2500	V = -0.0593	
		P	0.4598	0.4055	0.2500	W = 0.3342	$R_p = 27.2$
		O1	0.3587	0.5669	0.2500	X = 0.3526	$R_{wp} = 27.1$
		O2	0.5791	0.5195	0.2500	Y = 0.0000	$R_{exp} = 11.14$
		O3	0.3149	0.3114	0.1770		$\chi^2 = 5.90$
		O-H	0.0000	0.0000	0.0000		
		H	0.0000	0.0000	0.0000		
	$CaCO_3P_3$ (Trigonal System)-2	Ca	0.0000	0.0000	0.0000	U = 0.0041	
		C	0.0000	0.0000	0.2500	V = -0.0076	
		O1	0.1544	0.0000	0.2500	W = 0.0063	
						X = 0.0440	
						Y = 0.0000	
	$Ca_4H_4O_{16}P_4$ (Triclinic System)-2	Ca1	0.3219	0.5093	0.2642		
		Ca2	0.3219	0.5093	0.2642		
		P1	0.1948	0.3265	0.7122		
		P2	0.3187	0.9778	0.1873		
		O1	0.3435	0.3082	0.9994		
		O2	0.4559	0.6705	0.6804	U = 0.3884	
		O3	0.1578	0.2262	0.6521	V = -0.0209	
		O4	0.0229	0.5918	0.7245	W = 0.0139	
		O5	0.1607	0.8276	0.0069	X = 0.2345	
		O6	0.5220	0.1594	0.2968	Y = 0.0000	
		O7	0.0994	0.0673	0.1637		
		O8	0.3249	0.7664	0.3754		
		H1	0.0000	0.0000	0.0000		
		H2	0.4605	0.2588	0.9506		
		H3	0.5293	0.1160	0.4683		

Table 2: Rietveld refined parameters of functional magnetic nanoadsorbents: 1-monophasic and 2-multiphasic sample.

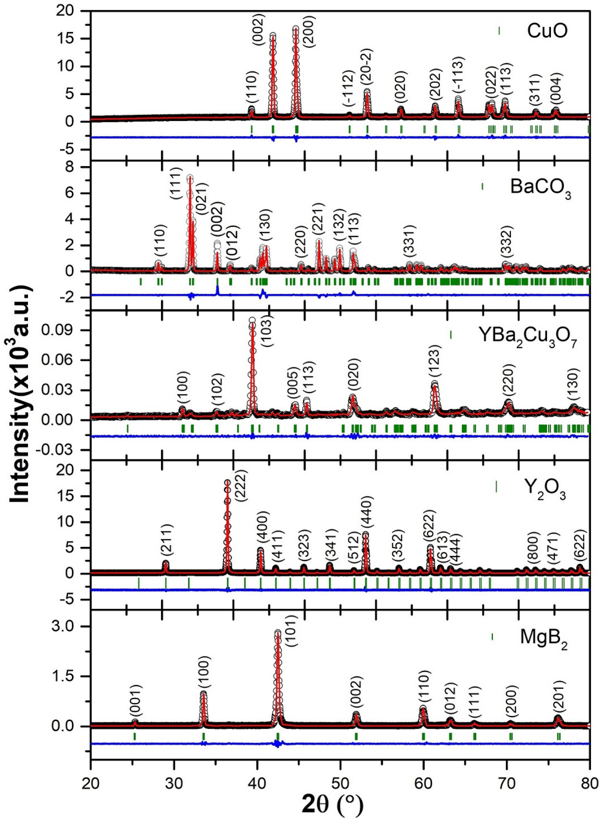

Figure 1: Refined diffractograms of precursors and superconducting samples, black circles represent data points, red lines are calculated diffractograms, and blue lines are their difference.

Figure 3 shows the 3D electronic densities from the results of the refinement of each sample, where the colors indicate electronic density; hence, atomic positions. Thus, it was demonstrated that a correct Rietveld refinement can provide many analytical products such as refined diffractograms, crystallite sizes and strains, phase contributions, electronic densities, and atomic structures, by configuring the outputs in FULLPROF Suite. These results are obtained from the XYN, MIC, PCR, INP, and CIF extension files. It must be noted that the IRF and the indexed sample's CIF were fundamental in order to obtain these results.

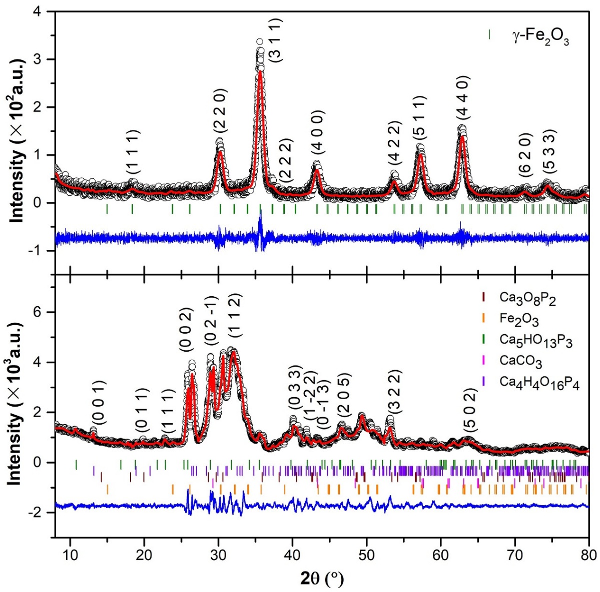

Figure 2: Refined diffractograms of functional magnetic samples: γ-Fe$_2$O$_3$ and MPS, black circles represent data points, red lines are calculated diffactograms and blue lines are their difference.

Conclusions

The Rietveld refinement method with FULLPROF Suite got presented and explained practically together with the involved parameters. It got successfully applied on superconducting samples and the functional magnetic nano adsorbents. In all this process, a novel, basic, and useful refinement protocol was developed along with pertinent advice. After samples refinement, many products, such as microstructural and crystallographic phase parameters, electronic densities, and atomic structure were obtained.

As a final note for new users of Rietveld refinement, it was observed that sometimes the protocol will not be enough to get good refinements, so the users need to read the provided theory in order to understand the functioning of the Rietveld method and the software at hand. That way, and by practice, users will obtain powerful knowledge and ability that will allow them to proceed in the refinements with their own criteria.

Sample		Cristallite Size (nm)	Strain (%)	Phase contribution (%)
CuO		1053.1	12.0	100
Y_2O_3		82.6	3.6	100
$BaCO_3$		73.4	11.9	100
$YB_2Cu_3O_7$		603.2	23.0	100
MgB_2		63.3	11.0	100
Fe_2O_3		20.4	32.3	100
Multiphasic Sample	$Ca_3O_8P_2$	67.4	21.2	4.99
	Fe_2O_3	20.0	3.9	0.80
	$Ca_5HO_{13}P_3$	611.6	28.9	49.84
	$CaCO_3$	18.8	5.1	3.01
	$Ca_4H_4O_{16}P_4$	2236.3	40.0	41.37

Table 3: Microstructural parameters of the refined samples.

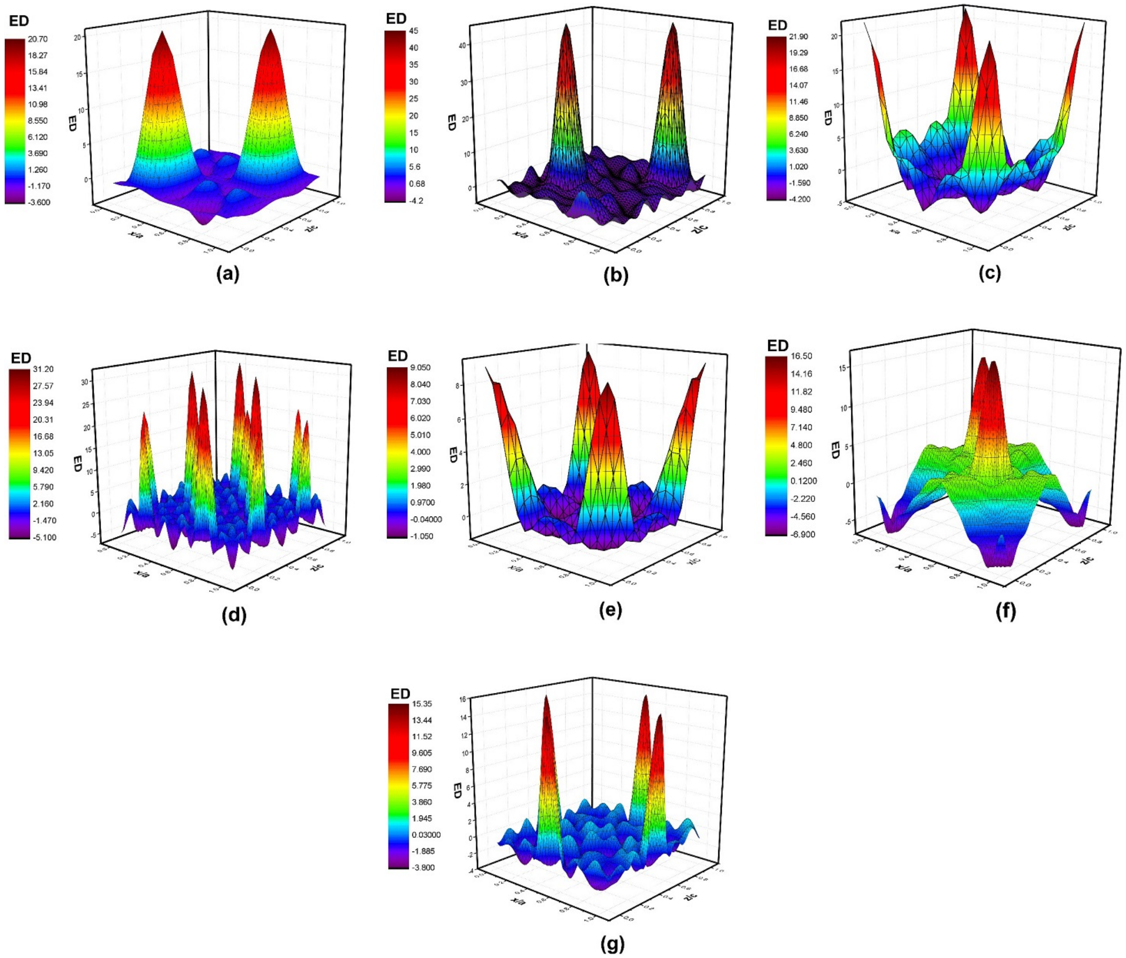

Figure 3: 3D electronic densities of (a) CuO, (b) $BaCO_3$, (c) $YBa_2Cu_3O_7$, (d) Y_2O_3, (e) MgB_2, (f) MPS and (g) Fe_2O_3, the ED axes indicate electronic density and the others represent spatial distribution.

Appendix A

Advises and suggestions for Rietveld refinement:

- When the background starts too out of line, it is suggested to refine it first or use linear interpolation with background points.
- When using linear interpolation with background points, it is possible to get negative values after their refinement. In these events, we suggest turning them back and not refining them in a while.
- Sometimes, after refining the FWHM parameters or the shape parameters, one could see a message that says: "WARNING: negative Gaussian FWHM somewhere in the pattern." In those cases, some of these parameters have wrong values, and one must avoid this by typing them or changing the order of refinement.
- It is strongly suggested to regularly save the progress during the refinement, i.e. make backups.
- When refining the thermal factors, occupancies, or the Cagloitti's coefficients, one could try to avoid some values with non-physical sense by using the restraints button in the PCR editor to forbid it.
- The Cagliotti parameters, U and V, vary the peaks broadening depending on their angular positions. Meanwhile, W uniformly modifies them.

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