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Relative recoilless F-factors in $REFeO_3$ (RE = rare-earth La, Pr, Nd and Sm) orthoferrites synthesized by self-combustion method

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ABSTRACT

In this work, rare-earth orthoferrites polycrystalline compounds $REFeO_3$ (REFO) with RE = rare-earth La, Pr, Nd and Sm were synthesized by the self-combustion method. A direct correlation between the magnitude of the magnetic hyperfine field and the Fe—O_1—Fe bond angles was observed. From transmission Mössbauer spectra recorded at room-temperature, relative recoilless F-factors for these REFO compounds were estimated. The method applied to perform this calculation was based on the determination of two subspectral areas present in a mixture of known amounts of the compound under study and a standard sample (α-Fe). For that purpose spectra were thickness-corrected and fitted using lorentzian lines. The so obtained factors were F-$_{REFeO3}$ (RE = rare-earth La, Pr, Nd and Sm): 1.30 ± 0.02, 1.08 ± 0.04, 1.15 ± 0.05, 1.18 ± 0.08 respectively. The absolute recoilless factors obtained by this method had an average relative error around 11% in comparison with the values predicted by the Debye model.

1. Introduction

The rare-earth orthoferrites $REFeO_3$ (REFO) are a family of oxides with distorted perovskite structure which show unusual and interesting magnetic properties [1,2]. These materials are canted antiferromagnets and have attracted much attention; first, for their special antisymmetric exchange interaction, which results in weak ferromagnetism [3], and second, for their potential use in spintronic applications (spin valves, sensors) [4,5], as they show spin reorientation phenomena induced by temperature or by an applied magnetic field [6–9]. Moreover, it is worth noting that one of the main components of the orthoferritas are the rare earths elements (REE) such as La, Pr, Nd, and Sm. Nowadays the REE, due to their unique electronic structure and the unique properties of the 4f electron orbitals, are very important elements for industry and have several applications in multiple fields. However, the world is passing by a crisis related with the demand and supply of REE due to their scarceness and how are distributed the REE deposits. Because of the absence of primary deposits to exploit on their territory, many countries will have to draw on recycling of REE from industrial residues and REE-containing end-of-life products. Nevertheless in spite of their importance in the electronic devices REE constitute a small fraction of weight/volume of a final product. In consequence, the exploit percentage is about the same as the poorer ore bodies (i.e., ~2%) from where REE are mined. In this sense a good tool to detect, identify and quantify rare-earth orthoferrites in samples of complex composition is quite desirable and useful [10,11]. Taking into account the above and considering the interesting magnetic properties of REFO compounds, most of the Mössbauer spectroscopy studies on orthoferrites have been focused on the comprehension of their weak ferromagnetism and the temperature dependence of the sublattice magnetization [12]. These compounds are magnetically ordered over a wide range of temperatures and therefore their Mössbauer parameters differ between the individual species. Thus, the technique is frequently used for the unequivocal distinction and detection of minor amounts of iron oxides, and often for its quantification in systems of complex compositions, taking advantage of the insensitivity of Mössbauer spectroscopy to all isotopes, except those under interest [13]. However, for quantitative Mössbauer characterization of a sample in which two or more iron compounds are present, it is necessary to take into account the recoil-free fraction (f) of each phase. This parameter is defined as the probability of a nucleus in a specific environment at a given temperature to present absorption and emission of gamma rays without recoil [14].

The recoilless f-factor can be calculated by using three methods: (1) the temperature dependence of the absolute subspectral area (A), (2) the temperature dependence of the isomer shift (δ), and (3) the ratio of subspectral areas of two different materials at a given temperature, one of these used as a reference. Methods (1) and (2) usually use the Debye model. For example, Eibschütz

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et al. [7] collected the Mössbauer spectra of the orthoferrites at different temperatures and studied the temperature dependence of the hyperfine parameters, and by using the Debye method, they derived the Debye temperature (θ_D). On the contrary, method (3) does not depend of the lattice vibration model, and the relative recoilless F-factors is obtained. This last method has been proven to be comparatively much simpler [13–19]. In our work, we use method (3). In this sense, the aim of this work was to find the room-temperature relative recoilless F-factors of four oxide compounds of the rare-earth orthoferrite family REFO (RE = rare-earth La, Pr, Nd and Sm) relative to α-iron which is commonly used as reference for these calculations. Compounds were synthesized by a self-combustion method and then characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy X-ray dispersive spectroscopy (EDX) measurements. Then, a discussion was made on the possible relation between their structural nature and the values of F-factors. Finally, with the idea of evaluating the effectiveness of this method, the *f* fractions derived from this calculation were compared to those calculated using the Debye temperatures previously reported in literature for these compounds [12].

2. Theory

Using the Debye approximation the probability of recoil-free emission or absorption events (*f*) can be described by the following equation [13,16]:

$$f = exp - \left\{ \frac{3E_\gamma^2}{k_B M \theta_D c^2} \left[\frac{1}{4} + \left(\frac{T}{\theta_D} \right)^2 \int_0^{\theta_{D/T}} \frac{xdx}{e^x - 1} \right] \right\} \tag{1}$$

where E_γ, k_B, M, θ_D, c, and T are the gamma ray energy, the Boltzmann's constant, the mass of the iron ^{57}Fe nucleus, Debye temperature, the speed of light, and the temperature, respectively.

As can be seen in Eq. (1), *f* is closely related to the strength of the atomic bonding and the vibrations in the solid, in which the Mössbauer nucleus is embedded [17] and it is clear that as the Debye temperature of the crystal becomes higher, *f* becomes higher as well [18]. This means that at a given temperature, the probability of a compound to show recoil-free emission or absorption events increases with the strength of bonds [19].

As has already been mentioned, the use of the Debye approximation to calculate *f* is complicated because it implies collecting several spectra under different temperatures, adjusting the temperature dependence of the isomer shift (δ) or of the subspectral area (A) to calculate the Debye temperature and finally, replacing it in Eq. (1). In comparison, determining the relative recoilless fraction (F) implies an easier procedure, since F is defined as the ratio of the recoil free fractions of two different materials. When the thin absorber condition is satisfied, the subspectral areas (*A*) are proportional to the product of the number of ^{57}Fe atoms (*N*) and the recoil-free fraction (*f*) of each compound [15].

$$\frac{A_a}{A_r} = \frac{f_a N_a}{f_r N_r} \tag{2}$$

$$F_a = \frac{f_a}{f_r} = \frac{A_a N_r}{A_r N_a} \tag{3}$$

where F_a is the relative recoilless fraction of the compound *a* with respect to a reference compound *r* and f_i, A_i, N_i are the recoil free fraction, the Mössbauer sub-spectral area and the total number of ^{57}Fe atoms in the ith-compound, respectively. N_i can be estimated as follows [15]:

$$N_i = \frac{a m_i O_i N_0 N_{i,m}}{MW_i} \tag{4}$$

where a, m_i, O_i, N_0, $N_{i,m}$ and MW_i are the natural abundance of ^{57}Fe ($a = 0.0217$), the mass of the compound, the occupancy fraction, the Avogadro's constant ($N_0 = 6.022 \times 10^{23}$ mol^{-1}), the number of iron atoms per unit formula and the molecular weight, respectively. In this case, the final expression for the F-factor of the REFeO$_3$ orthoferrites (F_{REFO}) relative to alpha-iron (α-Fe) as a function of their sub-spectral areas was obtained by replacing Eq. (4) in (3), thus:

$$F_{REFO} = \frac{m_{\propto Fe} A_{REFO}}{m_{REFO} A_{\propto FE}} C_{REFO} \tag{5}$$

$$C_{REFO} = \frac{O_{\propto Fe} N_{\propto FE,m} MW_{REFO}}{O_{REFO} N_{REFO,m} MW_{\propto Fe}} \tag{6}$$

where $m_{\alpha Fe}$, $O_{\alpha Fe}$, $N_{\alpha Fe}$, and $MW_{\alpha Fe}$ are the mass, the occupation fraction, the number of Fe atoms per unitary formula and the molecular weight of alpha-iron, respectively. On the other hand, m_{REFO}, O_{REFO}, N_{REFO} and MW_{REFO} are the mass, occupation fraction, the number of Fe atoms per unitary formula and the molecular weight of the orthoferrite REFO, respectively. $A_{\alpha Fe}$ and A_{REFeO3} are the alpha- iron and the orthoferrite sub-spectral areas, respectively. By assuming that the values for the occupation fractions of the alpha-iron and orthoferrites are equal to one, the Fe atoms by unitary formula of the alpha-iron and the orthoferrites are also equal to one and by introducing the molecular weights of the compounds (see Table 1); thus, four simple formulas were obtained to determine F_{REFO}.

3. Experimental

3.1. Synthesis method

All samples were synthesized by self-combustion method. Aqueous solutions in the adequate stoichiometry for each one of the rare-earth nitrates, plus iron nitrate were prepared. The nitrates used were $La(NO_3)_3 \cdot 6H_2O$ (Rodia), $Pr(NO_3)_3 \cdot 6H_2O$ (Rodia), $Nd(NO_3)_3 \cdot 6H_2O$ (Rodia), $Sm(NO_3)_3 \cdot 6H_2O$ (Rodia), and $Fe(NO_3)_3 \cdot 9H_2O$ (Aldrich). Acting as an ignition promoter, glycine $H_2NCH_2CO_2H$ (Merck) was added at the required amounts to get a molar ratio of $NO_3/NH_2 = 1$, which is a proper concentration to guarantee the total formation of complexes with metal cations while increasing their solubility and preventing selective precipitation. The resulting solutions were slowly evaporated at ~400 K until vitreous gels were obtained. The gels were heated up to approximately 550 K when an auto ignition reaction and rapid combustion took place, producing powdered precursors which might still contain carbon residues. Calcinations at 900 K for 10 h were performed to eliminate all the remaining carbon (if there was any) and promote the crystallinity.

3.2. Characterization

Structural properties and phase control were analyzed through X-ray diffraction patterns, which were taken using a Panalytical X́PERT PRO MPD diffractometer with CuK$_{\alpha1}$ radiation (1.5406 Å), operated at 45 kV and 40 mA. The diffraction patterns were recorded at intervals (2θ) from 10° to 90° with a scanning step size of 0.013° during 59 s per step. Rietveld refinement was done by using FullProf software with 22 parameters refined.

Table 1
Molecular weights and C_{REFO} values from Eq. (6) for α-iron and rare-earth orthoferrites REFO ($LaFeO_3$ = LFO, $PrFeO_3$ = PFO, $NdFeO_3$ = NFO, $SmFeO_3$ = SFO).

Compound	α-Fe	LFO	PFO	NFO	SFO
MW_n [g/mol]	55.9	242.8	244.8	248.1	254.2
C_{REFO}	1	4.35	4.38	4.44	4.55