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Is $Sm_3Fe_5O_{12}$ Really Cubic at Room Temperature ?

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Abstract

A sample of $Sm_3Fe_5O_{12}$ was sintered from corresponding mixed hydroxides that were obtained by coprecipitation of mixed nitrates. The x-ray diffraction experiment was done with monochromatized CuK_α radiation at room temperature. The sample crystallizes in the garnet structure type. The iron ions occupy both the tetrahedral and octahedral positions, while the samarium cations occupy the dodecahedral position. The refinements were done in the cubic space group Ia3d and the rhombohedral space group R-3c with a hexagonal axis. Note that the group R-3c is a subgroup of the symmetry group of the magnetic moment and subgroup of the Ia3d group. The transformation of the refined atomic coordinates from the group Ia3d into the group R-3c gives the same values, within the sum of standard deviations, as the values obtained from the refinement in the rhombohedral space group. The Debye temperatures, obtained from thermal displacement B-factors, are 320 and 560 K from the refinements in the cubic and the rhombohedral space group, respectively. The later temperature agrees with the Debye temperature obtained by independent measurements.

Key words: Garnets, x-ray diffraction, symmetry, Debye temperature

1. Introduction

Since their discovery, magnetic garnets have played an important role in basic and applied science [1]. Their importance is based on their applicability for different magnetic media. On the other hand, these compounds are a test for Neel's theory of ferrimagnetism.

$Sm_3Fe_5O_{12}$ (SmIG) belongs to the family of rare earth magnetic garnets whose prototype is the ferrimagnetic $Y_3Fe_5O_{12}$ [1]. In the garnet structure, the space group Ia3d in the paramagnetic phase, the yttrium or rare earth ions occupy the special position 24c, with dodecahedral coordination, the iron ions occupy the special 24d sites, with tetrahedral coordination and the 16a position with octahedral coordination, and all oxygen ions are in the general 96h position [1]. The unit cell contains eight formula units.

From the theoretical point of view, there is no doubt that the garnet structure below the Curie point, about 560 K for all rare earth iron garnets (REIG) and yttrium iron garnet (YIG), can not be cubic. Namely, the existence of the ordered magnetic phase requires a lowering of symmetry, according to the Curie principle [2]. However, the YIG and REIG structures are described in the cubic system at room temperature [3]. Only at low temperatures some REIG structures, which exhibit additional reflections in comparison with Ia3d reflections, are described in the rhombohedral space group [4]. It has been recently shown that, even if the new reflections do not appear as in the case of the YIG and yttrium aluminum iron garnet, only description in the rhombohedral space group gives the magnetic moment and Debye temperature in agreement with independent experiments [5,6].

In this work our intention is to check whether the SmIG is really cubic at room temperature. SmIG cannot be investigated by neutron diffraction, due to the giant absorption of neutrons by Sm. For that reason we have performed x-ray diffraction measurements.

2. Experimental

A powder sample of $Sm_3Fe_5O_{12}$ was sintered from corresponding mixed hydroxides that were obtained by coprecepitation of mixed nitrates. The presintering was done at temperature 950°C for 24 hours. The sample was cooled and subsequently pressed to a pressure of 1.5 t/cm^2 and refired at 1350°C for 8 hours in order to get samples of higher density.

The x-ray diffraction data for the Rietveld analysis of $Sm_3Fe_5O_{12}$ sample were collected by a Philips PW1710 powder diffractometer with graphite monochromatized CuK_α radiation at ambient temperature. The scanning 2θ range was $9-135°$, with the scanning time of 15 s per step and a step width of 0.02°. This experiment confirmed the garnet phase without impurities.

3. Results

The crystal structure was refined by the Rietveld profile method with the use of the Fullprof program [7]. At first the crystal reflections were indexed in the space group Ia3d. In this space group all cations occupy special positions: the yttrium ions are in the 24c positions whose local symmetry is 222, the iron ions are in the 16a and 24d positions with site symmetries -3 and -4, respectively. Only the oxygen ions in the general 96h positions, local symmetry 1, have three degrees of freedom.

The starting model for the refinement procedure was the refined crystal structure of $Tb_{2.5}Y_{0.5}Fe_5O_{12}$ [8]. The assumed peak shape corresponded to the pseudo-Voigt function.

In the last cycle of the refinement of $Sm_3Fe_5O_{12}$, total of 19 parameters were varied: one scale factor, one zero point, one mixing parameter, one asymmetry and one preferred orientation parameter, three parameters for the description of the background, three parameters for the halfwidths description and the lattice constant parameter. The atomic parameters were three free coordinates of the oxygen anion and four displacement B factors - one for each ion at four different crystallographic positions. 152 reflections were used in the refinement.

The space group R-3c was also used for the refinement. In this space group, the starting lattice constants and coordinates were obtained by transforming refined lattice parameters and coordinates from the space group Ia3d. Two hexagonal axes of the rhombohedral cell are the face diagonals of the cubic cell and the third is one half of the body diagonal. In the group R-3c, samarium ions occupy two dodecahedral 18e sites, iron ions occupy 6b

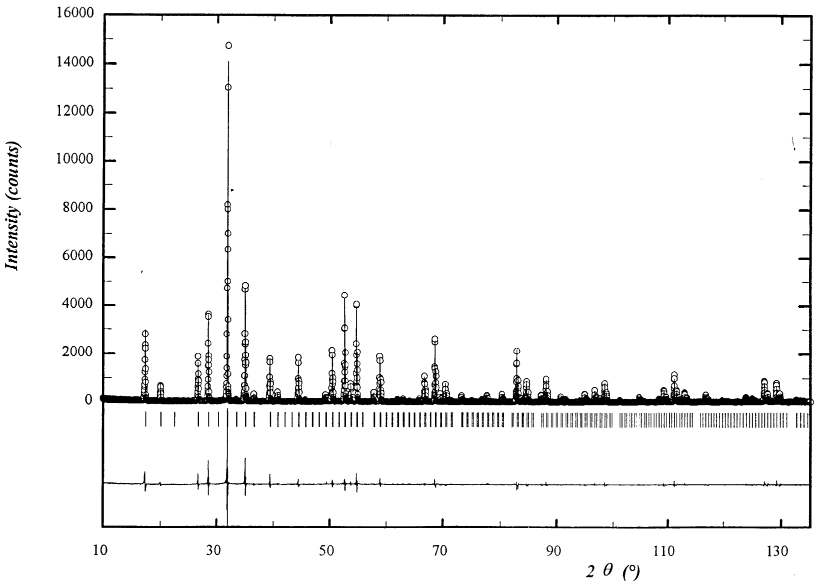

Figure 1. Observed (points) and calculated (line) x-ray diffraction pattern of $Sm_3Fe_5O_{12}$ by using space group R-3c. The line at the bottom represents the difference between observed and calculated values.

and 18d octahedral positions as well as 36f positions. The oxygen ions are in four 36f sites. In the last cycle of the refinement in this space group, a total of 32 parameters were varied: one scale factor, one zero point, one mixing parameter one asymmetry and one preferred orientation parameter, three parameters for the description of the background, three parameters for the halfwidths description and two lattice constant parameters. The atomic parameters were three free coordinates of iron in 36f positions, altogether 12 free coordinates of the oxygen anions for four oxygens in 36f sites, and four displacement *B* factors - one for samarium cations in dodecahedral positions, one for iron in tetrahedral sites, one for iron in octahedral positions and one for oxygen ions. 626 reflections were used in this refinement.

The parameters of the crystal structure are listed in Tables 1. and 2.

Table 1. The atomic parameters from the Rietveld refinement of $Sm_3Fe_5O_{12}$ by using space group Ia3d.

a [Å]	12.53255(9)
O_x	-0.0303(6)
O_y	0.0529(9)
O_z	0.1494(7)
$B_{Fe,octa}$ [Å^2]	0.24(7)
$B_{Fe,tetra}$ [Å^2]	0.45(6)
B_{Sm} [Å^2]	0.34(3)
B_O [Å^2]	1.0(2)
R_B [%]	6.94
$R_{Exp.}$ [%]	10.03
R_P [%]	17.4
R_{WP} [%]	22.5

Table 2. The atomic parameters from the Rietveld refinement of $Sm_3Fe_5O_{12}$ by using space group R-3c.

a [Å]	17.7250(3)			
c [Å]	10.8519(4)			
atom	x	y	z	B [Å ^{2}]
Fe, octa	0	0	0	0.23(6)
Fe, octa	0.5	0	0	0.23(6)
Fe, tetra	0.209(2)	0.166(2)	0.419(3)	0.38(8)
Sm	0.625	0	0.25	0.35(3)
Sm	0.125	0	0.25	0.35(3)
O1	0.337(4)	0.566(3)	0.776(6)	0.2(2)
O2	0.747(3)	0.817(4)	0.415(7)	0.2(2)
O3	0.748(4)	0.715(5)	0.617(6)	0.2(2)
O4	0.149(5)	0.884(6)	0.184(6)	0.2(2)
R_B [%]	7.02			
$R_{Exp.}$ [%]	10.56			
R_P [%]	17.8			
R_{WP} [%]	22.6			

4. Discussion

The atomic coordinates obtained in the space group Ia3d can be transformed into the atomic coordinates in the group R-3c. The transformed coordinates are the same, within the sum of standard deviations, as the refined coordinates in the group R-3c.

The samarium ion is coordinated with four oxygen ions at 2.41 Å and four oxygen ions at 2.52 Å. If one takes an oxygen radius of 1.40 Å, the radius of the samarium ion is 1.01 Å. The tetrahedral iron is surrounded with four oxygens at the distance of 1.85 Å. This distance corresponds to the oxygen radius of 1.40 Å and high spin radius of Fe^{3+} of 0.47 Å in tetrahedral position. There are 6 oxygens around the octahedral site at 2.02 Å. This distance corresponds to the high spin ferri radii of 0.62 Å. The literature values of ionic radii in the garnet structure for Sm^{3+} and Fe^{3+} in tetrahedral and octahedral sites are 1.04 Å, 0.49 Å and 0.64 Å, respectively [9]. Note that the here obtained values of radii are somewhat smaller than those from literature which indicates a small presence of the covalent bond.

In the space group Ia3d, the B factors for the oxygen anions are always larger than the B factors for the cations, as expected. The B factor for the heaviest Sm ion is notthe smallest, unexpectedly. This means that in this compound the strength of the bonds affects the B factors. By using expression for the mass averaged B factor [10]:

$$\bar{B} = \frac{6h^2}{m_a k_B \theta_D}\left[\frac{\Phi(x)}{x} + \frac{1}{4}\right] \tag{1}$$

where h represents Planck's constant, m_a average atomic weight, k_B Boltzmann's constant, θ_D the characteristic Debye's temperature, x the ratio of θ_D to absolute temperature and $\Phi(x)$ is Debye's integral, the characteristic Debye's temperature is found to be 320(40) K.

This result is in big disagreement with independent determination of θ_D, from thermal expansion of lattice parameters, which gives the value of 540 ± 30 K [11].

In the space group R-3c the B factor of oxygen ions is the smallest one. However, this can be true if the oxygen ions are strongly bonded to metallic ions. For this case θ_D is also calculated from equation (1). It was found that θ_D is 560(60) K. This result is in full agreement with the already mentioned result: 540 ± 30 K [11].

All R factors are slightly better for the refinement in the cubic space group. Also note that refinement in the Ia3d space group was done with less parameters than in the group R-3c.

An attempt was also made to refine crystal structure of magnetically ordered $Sm_3Fe_5O_{12}$ in the space group R-3. Note that the crystal and magnetic structure of $Y_3Fe_5O_{12}$ has been already refined in this space group [5], which is a subgroup of the group R-3c. However, these attempts were not successful, after many cycles the refinements did not reach a convergence.

5. Conclusion

There is no doubt that refinement in the cubic space group, characterized by smaller R factors and a less number of parameters, is better than the refinement in the rhombohedral space group. However, the refinement in the rhombohedral space group cannot be rejected from two reasons. The first is that theoretically the magnetically ordered sample can not be cubic [2]. In this case the magnetic moments oriented along the body diagonal in the cubic system require a rhombohedral space group. The other reason is agreement of the Debye's characteristic temperature from independent measurements only with the refinements in the rhombohedral space group. This temperature is between 500 and 600 K for all REIG and YIG [11]. The neutron diffraction measurements of mixed yttrium aluminum iron garnet showed that this sample, which is rhombohedral at low temperatures approaches cubic symmetry with an increase of temperature [6]. In the case of SmIG it seems that the cubic model better fits the experimental x-ray diffraction data but the rhombohedral model better describes Debye's temperature, i.e. a coarse description of lattice dynamics is better in the rhombohedral model.

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