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Mössbauer and magnetic investigation of scandium and indium substituted $PbFe_{12}O_{19}$ hexagonal ferrite

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Magnetic and Mössbauer measurements have been performed on polycrystalline substituted M-type hexagonal ferrites of compositions $PbFe_{12-x}Sc_xO_{19}$ ($x = 0$, 0.5, 1, 1.5) and $PbFe_{12-x}In_xO_{19}$ ($x = 0$, 1, 2). The substitution of the Fe^{3+} by Sc^{3+} and In^{3+} ions perturbs the axial magnetic order giving rise to angled magnetic structures. From the values of the quadrupole splitting of the Fe^{57} 14.4 keV level, measured above and below the Curie temperatures, the angle between the magnetic moment of the Fe^{3+} ions in various sublattices and the hexagonal *c*-axis have been deduced. At 77 K the measured angles do not exceed 20° and depending on *x* are different for different sublattices. The dependence of *x* on the saturation magnetisation at 0 K, expressed in Bohr magnetons, differs markedly in Sc and In containing compounds, partly due to the different substitution probability of iron in the spin up and spin down sublattices, and also due to the different spin canting angles.

1. Introduction

Early studies of the magnetic order in $BaFe_{12-x}Me_xO_{19}$ (Me = Sc, In) single crystals using neutron diffraction technique suggest the formation of angled magnetic structure induced by the substitution of Fe^{3+} by Sc^{3+} and In^{3+} ions. Helical block magnetic structure was found in $BaFe_{12-x}Sc_xO_{19}$ [1] and block angled order in $BaFe_{12-x}In_xO_{19}$ compounds [2]. The onset of such peculiar magnetic structures is associated with the order of substitution of iron in the various sublattices and with the local perturbation of the magnetic interactions that, in turn, can be influenced by the type of heavy bivalent cations (Ba, Sr or Pb) present in the compound. Moreover, because of the electronic structure of Pb^{2+}, the substituted Pb ferrites may show magnetic behaviour different from that revealed in the analogous Ba or Sr compounds.

In the present work we report and discuss the results of magnetic and Fe^{57}-Mössbauer absorption measurements on $PbFe_{12-x}Sc_xO_{19}$ ($x = 0$, 0.5, 1, 1.5) and $PbFe_{12-x}In_xO_{19}$ ($x = 0$, 1, 2) polycrystalline samples. The information deduced from the Mössbauer data is not in itself sufficient for a full understanding of the magnetic structure, as would be possible by neutron diffraction measurements on single crystal specimens. However, the data obtained do give evidence of the onset of angled spin ordering in the compounds with $x \geq 1$, allowing the determination of the angle between the Fe^{3+} magnetic moments in some sublattices and the hexagonal *c*-axis. The deduced canting angles are in agreement with the measured values of the saturation magnetisation.

2. Experimental

Polycrystalline samples of $PbFe_{12-x}Sc_xO_{19}$ ($x = 0, 0.5$, 1, 1.5) and $PbFe_{12-x}In_xO_{19}$ ($x = 0$, 1, 2) were prepared by metallorganic decomposition: solutions of Pb, Fe, Sc and In nitrates in ethylene glycol were heated to induce a polymerisation and, subsequently, a pyrolysis to remove the organic material. The resulting powder was heated to 920 °C for 24 h in air. The homogeneity of the samples were checked by X-ray diffraction using Co K_α radiation, by Mössbauer measurements below and above the Curie temperature (T_C), and by thermomagnetic analysis (TMA). Any spurious phases in quantities greater than 5 wt% can be excluded. The saturation magnetisation (M_s) in the range of temperature 77–300 K was measured using an Oxford 3001 vibrating sample magnetometer ($H_{max} = 16$ kOe). Mössbauer absorption spectra of the Fe^{57} 14.4 keV γ-radiation were recorded using a 15 mCi Co^{57} source in a Rh matrix, with a spectrometer working at constant acceleration, and the absorber samples held at a fixed temperature in the range 77–800 K. The spectra were analysed using a programme with which it is possible to optimise the isomer shift, the quadrupole splitting, the hyperfine magnetic field (H_{hf}), and the intensity (I) of the subspectra corresponding to the various iron sublattices of the M-type structure. The intensities were calculated as the area submitted by lines with Lorentzian shape.

3. Results and discussion

All the examined samples show a well defined magnetic order-disorder transition. The Curie temperatures (T_C) decreased linearly with increasing x (Fig. 1). The values determined by Mössbauer measurements are in good agreement with those deduced by the thermomagnetic analysis.

It should be noted that in the crystal structure of the M-type hexagonal ferrite, the 12 Fe^{3+} ions per unit formula are distributed amongst five sublattices. Six occupy the octahedral sites, k (spin up), at the interface between the spinel (S) and the hexagonal (R) structural blocks, one the octahedral, a, site (spin up) inside the S block, two the octahedral, f_{VI}, sites (spin down) inside the R block, two tetrahedral, f_{IV}, site (spin down) inside the S block, and one pseudo-hexahedral, b, site (spin up) inside the R block. This last one is so indicated because the cations are displaced from the symmetry plane of the trigonal bipyramid.

3.1. Mössbauer measurements

The Mössbauer spectra of substituted compounds both below and above the Curie temperature have been interpreted by comparison with the spectra of non substituted Pb ferrite looking at the evolution of the spectrum pattern with increasing x and applying the procedure previously followed for Al and Cr substituted Pb-hexaferrite [3, 4].

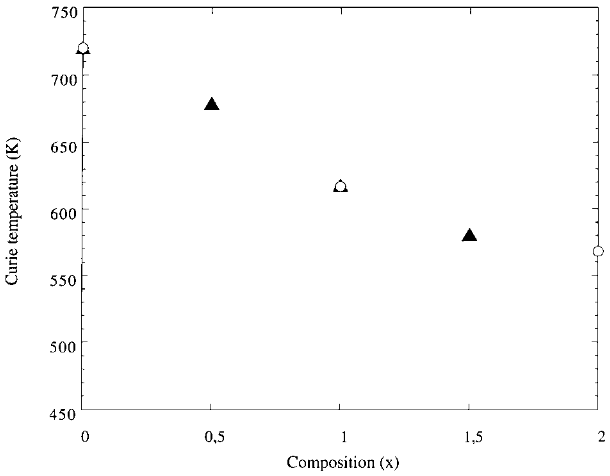

Figure 1 Curie temperatures for $PbFe_{12-x}Sc_xO_{19}$ (▲) and $PbFe_{12-x}In_xO_{19}$ (○) hexaferrites.

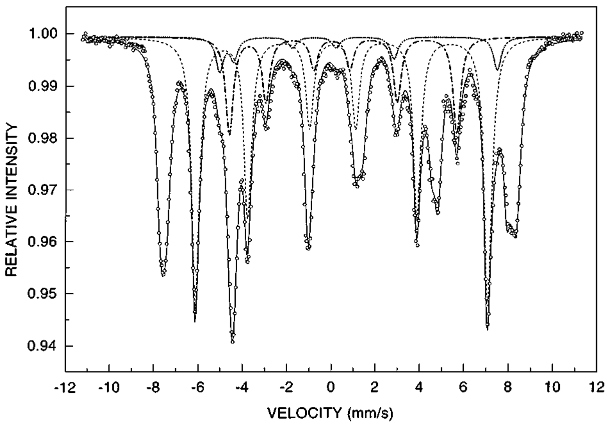

Figure 2 Fe^{57} Mössbauer spectrum of the $PbFe_{12-x}Sc_xO_{19}$ ($x = 0.5$) ferrite at $T = 295$ K. Experimental points (○ ○ ○); spectrum fitted as a superposition of five sextets (——); subl. k (---); subl. k' (_•_•_•_); subl. b (● ● ● ●).

The substitution of the Fe^{3+} by Sc^{3+} and In^{3+} strongly influences the temperature dependence of the magnetic moments of the non substituted Fe^{3+} ions in the sublattice k. In the Mössbauer spectra of substituted compounds at $T < T_C$ the nuclear Zeeman sextet of the k ions splits into different sextets ($k', k'', \ldots$) which corresponds to a lower hyperfine magnetic field. This is evident even at low x as shown in Fig. 2 for $PbFe_{12-x}Sc_xO_{19}$ ($x = 0.5$) at $T = 295$ K, where a sextet (k') appears besides the intense k sextet. With increasing x, the other sextets ($k'', k''', \ldots$) appear with their relative intensities increased. This phenomenon was also seen in Sc and In substituted Ba hexaferrite [5] and does not depend on the type of heavy divalent cations (Ba, Sr, Pb) present in the formula unit, but is related to the specific order of substitution of iron ions in different lattice sites for different substituting ions. It has been noted that it also takes place for Ga, but not for Al and Cr substituted M-type ferrites [3, 5]. The appearance of the sextets ($k', k'', k''', \ldots$) was interpreted as a consequence of the entrance of the substituting non magnetic ions into the f sublattices which are strongly magnetically coupled with the sublattice k. The Fe ions of these sublattices that have lost part of the superexchange interactions with the f ions show a more rapid decrease of their magnetic moment with increasing temperature.

In Figs 3 and 4 the temperature dependence of the H_{hf} values for the Fe^{57} nuclei in the various sublattices of $PbFe_{11.5}Sc_{0.5}O_{19}$ and $PbFe_{11}InO_{19}$ compounds are reported, respectively. The figures show clearly the different temperature dependence of the H_{hf} values for k and k' iron ions. In the spectra of $PbFe_{11}InO_{19}$ the definition of the lines of the sextet k' is less clear on the side of lower velocity indicating that the peaks of the sextet k'' start to be evident. However, due to their small intensity we were not able to get a satisfactory fit of the sextet k''. In the spectra of the Sc ($x = 1.5$) and In ($x = 2$) compounds the lines of the sextets k'' and k''' become relatively intense and the spectrum pattern at high temperatures looks very complex.

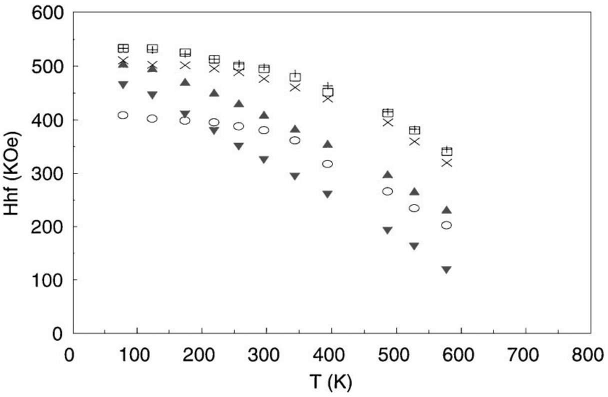

Figure 3 Temperature dependence of the hyperfine magnetic field at the Fe^{57} nuclei in the k (▲), k' (▼), a (□), b (○), f_{VI} (+) and f_{IV} (×) sublattices of $PbFe_{12-x}Sc_xO_{19}$ ($x = 0.5$) hexaferrite.

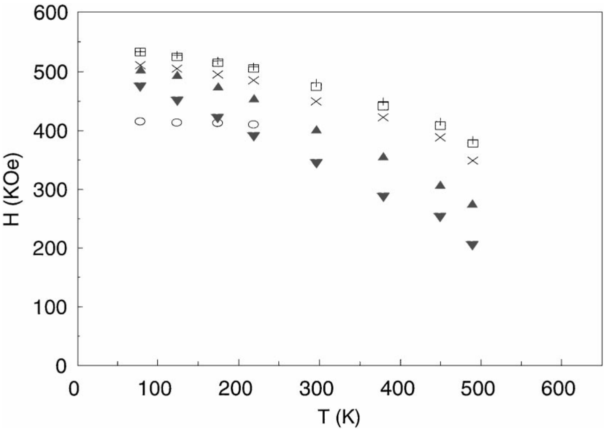

Figure 4 Temperature dependence of the hyperfine magnetic field at the Fe^{57} nuclei in the k (▲), k' (▼), a (□), b (○), f_{VI} (+) and f_{IV} (×) sublattices of $PbFe_{12-x}In_xO_{19}$ ($x = 1$) hexaferrite.

The main goal of the present Mössbauer investigation was to obtain information on the orientation of the magnetic moments of the non substituted iron ions. This was made by determining the values of the quadrupole splitting (QS) from the spectra, measured at temperatures below and above T_C, taking into account that at $T < T_C$ the quadrupole splitting of the Fe^{57} 14.4 keV level depends on the angle (φ) between the axis of the electric field gradient (V_{ZZ}) and the direction of the hyperfine magnetic field at nucleus as:

$$QS' = 1/2\, QS\, (3\cos^2\varphi - 1) \qquad (1)$$

where QS and QS′ denote the quadrupole splitting above and below T_C, respectively.

It is worth noting that in previous investigations of $PbFe_{12}O_{19}$ hexaferrites [3], a jump in the QS value for the k sublattice at $T = T_C$ has been observed. Due to the fact that the magnetic moments of the iron ions in the non substituted M-type ferrites are aligned along the hexagonal c-axis, an angle $\varphi = 23 \pm 2°$ between the c and the electric field gradient axis was determined for the iron ions in the octahedral sublattice k. This was considered calculating the angle (Θ) between the direction of the magnetic moment of Fe^{3+} ions belonging of the k sublattice and the c-axis in the substituted compounds. For the Fe^{3+} ions of the sublattice b the V_{ZZ} axis coincide with the hexagonal one and $\varphi = 0$.

As mentioned above, the Mössbauer spectra of the In and Sc substituted compounds, which are the result of the superposition of 6–8 sextets, appear to be very complex and their interpretation is not always straightforward. Therefore, we focused attention on the main intense sextets k for which an accurate determination of the quadrupole splitting is possible in a relatively large temperature interval. The sublattice b, in spite of its low relative intensity, was also considered because, due to its large quadrupole splitting, its subspectrum is clearly distinguishable at low temperatures and at $T > T_C$.

Good fitting of the spectra were obtained by adopting the same procedure described in Ref. [3] and assigning one doublet to all the Fe^{3+} ions of the sublattice k. In Fig. 5 the spectrum of $PbFe_{12-x}In_xO_{19}$ ($x = 2$) at $T > T_C$ is shown. In Fig. 6 the dependence of the quadrupole splitting for the sublattice b and k with x for both the Sc and In substituted compounds at $T > T_C$ is reported.

For $PbFe_{12-x}Sc_xO_{19}$ ($x = 0.5$) at T < T_C a satisfactory interpretation of the spectra is possible in nearly all the temperature intervals between 77 K and T_C. In Fig. 7 the temperature dependence of the QS for the sublattice b and k is reported. From 77 K to T_C the QS of the k sublattice slowly increases with T, with a temperature coefficient of 0.00007(1)/°C in agreement with our previous measurements for the non substituted Pb-ferrite;

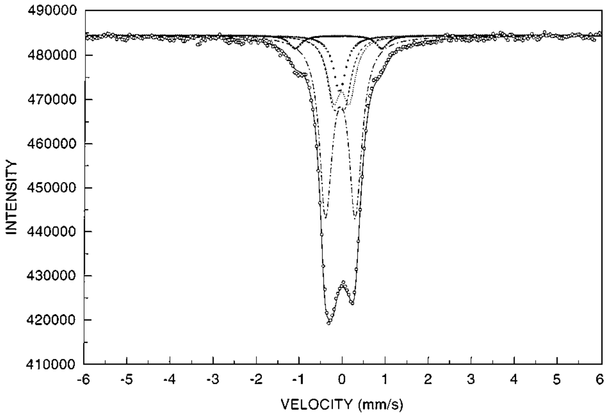

Figure 5 Fe^{57}-Mössbauer spectrum of $PbFe_{12-x}In_xO_{19}$ ($x = 2$) at $T = 753$ K. Experimental points (○ ○ ○); fitted spectrum (—); subl. k (_●_●_●_); subl. a (+++); subl. b (▲▲▲); subl. f_{VI} (●●●●); subl. f_{IV} (----).

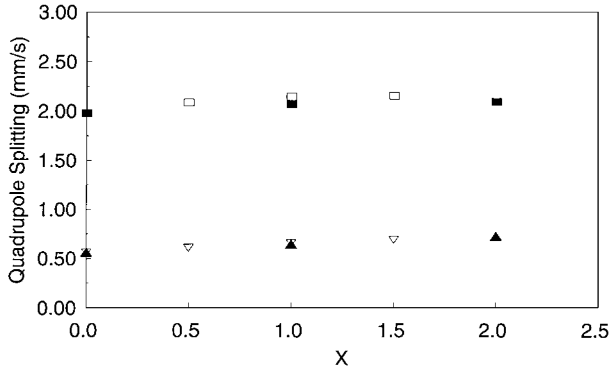

Figure 6 Quadrupole splitting for Fe^{57} nuclei in the sublattices k (▲) and b (■) of $PbFe_{12-x}In_xO_{19}$ and the sublattices k (▽) and b (□) of $PbFe_{12-x}Sc_xO_{19}$ compounds at $T > T_C$.

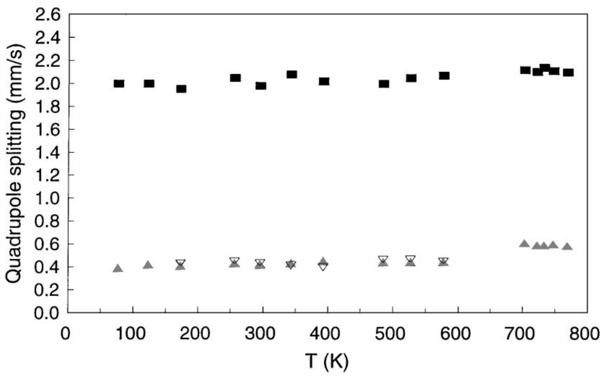

Figure 7 Temperature dependence of the quadrupole splitting for Fe^{57} nuclei in k (▲), k' (∇) and b (■) lattice sites of $PbFe_{12-x}Sc_xO_{19}$ ($x = 0.5$) ferrite at $T > T_C$.

crossing the Curie temperature a jump of the QS occurs, similar to that observed in $PbFe_{12}O_{19}$ [3]. From the QS values above and below T_C an angle $\varphi = 23 \pm 2^\circ$ between the c and the electric field gradient axis was calculated. It turns out to be equal to that of the non substituted Pb ferrite demonstrating that for $x = 0.5$, in the explored temperature range, the spin of the Fe^{3+} ions in the k lattice sites remains oriented parallel to the hexagonal c axis ($\Theta = 0$). Within experimental uncertainty the quadrupole splitting of the magnetically "weakened" (k') Fe^{3+} ions are equal to that of the "non weakened" k ions. No deviation from the c axis direction was detected for the magnetic moments of the Fe^{3+} ions in b lattice sites.

For the In and Sc substituted compound with $x = 1$ the subspectrum of the sublattice b is clearly distinguishable only at $T < 200$ K, while the subspectra due to the k ions are well defined up to $T \cong 400$ K. For $x > 1$, due to the superposition of the various subspectra, an accurate determination of QS for the b sublattice is possible only at temperatures near 77 K and for the k sublattice at $T < 300$ K.

For $PbFe_{12-x}Sc_xO_{19}$ and $PbFe_{12-x}In_xO_{19}$ ($x = 1$) the values of the QS of the sublattice k do not show any deviation from the light linear dependence on T. Using the formula (1) the angle φ between the direction of the H_{hf} and the V_{ZZ} axis was determined. Taking into account that the V_{ZZ} direction forms an angle of 23° with the c axis we calculated that the direction of the magnetic moment of Fe^{3+} ions belonging to the sublattice k at 77 K forms an angle $\Theta = 6 \pm 3^\circ$ and $4 \pm 3^\circ$ with the c axis in Sc and In bearing compounds, respectively. Possible changes in the Θ values between 77 and 400 K are within experimental uncertainty. As pointed out above an analogous temperature dependence for the QS value of the sublattice b was not obtained. For this sublattice an angle $\Theta = 10 \pm 2^\circ$ was calculated from the value measured at $T = 77$ K, corrected for the temperature factor determined for $x = 0$ and 0.5 and comparing it with the value measured at $T > T_C$. The same procedure was adopted to determine the angle Θ for Sc ($x = 1.5$) and In ($x = 2$) containing compound at $T = 77$ K. These were found to be $\Theta = 15 \pm 2^\circ$ and $18 \pm 2^\circ$, respectively.

In spite of the fact that the measured angles Θ are small, in some cases near the limits of the experimental sensibility, the Mössbauer data give evidence that the substitution of Fe^{3+} by Sc^{3+} and In^{3+} ions perturbs the collinear magnetic order, giving rise to a complex spin canting that persists in a large temperature interval over 77 K.

The analysis of the relative intensity of the subspectra corresponding to the various sublattices indicate that the Sc and In ions are substituting for the iron ions both in spin up and spin down sublattices with a light preference for the spin down f sublattices. We were not able to discriminate between the f_{IV} and f_{VI} lattice sites.

3.2. Magnetic measurements

The values of the saturation magnetisation are strongly influenced by the changes in the magnetic order. In Fig. 8 the temperature dependence of M_s for the Sc substituted compounds is reported. For $x = 0.5$ and $x = 1$ the $M_s(T)$ curves present a monotonic behaviour without changes in the slope so that a satisfactory extrapolation to 0 K can be obtained. In particular, for $x = 0.5$, taking into account that the Mössbauer data demonstrated that the Fe^{57} magnetic moments remain aligned along the c axis direction down to 77 K, the obtained value ($M_s(0) = 19.4\,\mu_B$) represents the saturation magnetisation at 0 K for the collinear axial spin order. From this value the distribution probability of Sc ions among the spin down and spin up sublattices was determined and utilised to calculate the dependence of $M_s(0)$ on x for a collinear spin arrangement (see Fig. 9). For $x = 1$ the value of $M_s(0) = 18.18\,\mu_B$, obtained by extrapolating to 0 K the experimental $M_s(T)$ curve is slightly lower than the calculated value ($M_s(0) = 18.8\,\mu_B$) for a collinear order. In fact the Mössbauer data show that, when the temperature reaches 77 K, a small deviation from the axial magnetic order takes place. The reported difference between the calculated and experimental $M_s(0)$ values corresponds to a mean angle Θ between the spin direction and the c axis at 0 K equal to $15 \pm 3\%$. It may be noted that for $BaFe_{12-x}Sc_xO_{19}$ ($x = 1.2$) at $T = 77$ K the formation of a block magnetic helix structure with a vertex angle of 15° is reported in the literature [1].

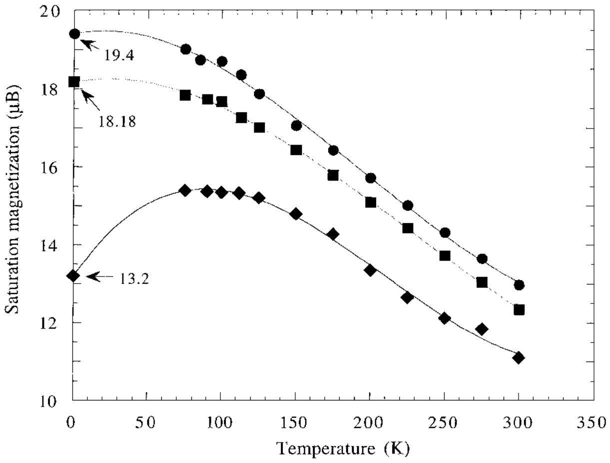

Figure 8 Temperature dependence of the saturation magnetisation (M_s) in Bohr magnetons per unit formula for the $PbFe_{12-x}Sc_xO_{19}$ compounds; (●) $x = 0.5$; (■) $x = 1$; (◆) $x = 1.5$.

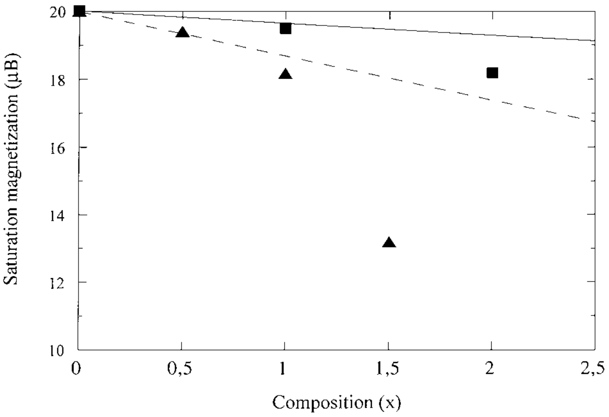

Figure 9 Saturation magnetisation ($M_s(0)$) in Bohr magnetons per unit formula for $PbFe_{12-x}In_xO_{19}$ (■) and $PbFe_{12-x}Sc_xO_{19}$ (▲) hexaferrites at $T = 0$ K. The full and the dotted lines denote the calculated values in the hypothesis of axial magnetic order for In and Sc containing compounds, respectively.

As shown in Fig. 8, the formation of angled spin structure influences the $M_s(T)$ curve for the sample with $x = 1.5$ already at T around 77 K by lowering the M_s values at $T < 77$ K. In this case the extrapolation to 0 K is not so straightforward as in the previous ones. However, by fitting the experimental data, an extrapolated value of $M_s(0) = 13.2 \pm 0.3$ μ_B was obtained corresponding to a mean angle $\Theta = 43 \pm 3°$ between the Fe^{3+} magnetic moments and the c axis at 0 K. For $BaFe_{12-x}Sc_xO_{19}$ ($x = 1.5$) at $T = 4.2$ K an angle Θ of 60° is reported in the literature [1].

An overall comparison of our results with data in the literature on Sc substituted Ba ferrite leads to the conclusion that in $PbFe_{12-x}Sc_xO_{19}$ for $x > 0.5$ the onset of angled spin structures takes place at lower T and with lower angles Θ between the direction of Fe^{3+} magnetic moments and the hexagonal c axis.

The values of M_s of the In containing compounds depend monotonically on T without discontinuities or drastic changes in the slope (see Fig. 10). In Fig. 11 the values of M_s measured at 77 K as a function of x are shown together with the analogous data for $BaFe_{12-x}In_xO_{19}$ reported in Ref. [6]; the values for $PbFe_{12-x}In_xO_{19}$ ($x = 1$, 2) are lower than the corresponding value of the substituted Ba ferrite. As shown in evidence by neutron diffraction investigations described in Ref. [2], the drastic change in the M_s values of $BaFe_{12-x}In_xO_{19}$ starting at $x \cong 2$ is due to the onset of block angled magnetic orders with the angle between the block magnetisation vector and the c axis equal to $15 \pm 2°$ for $x = 3.5$, $10 \pm 2°$ for $x = 3$ and less than 10° for $x = 2.5$. Our Mössbauer data show that in $PbFe_{12-x}In_xO_{19}$, also at $x = 1$, deviation from the collinear order takes place. However, the spin canting angles are so small that they can induce a reduction of the projection of the magnetic moments to the c axis direction of less than 2%. This is confirmed by the extrapolated value of the saturation magnetisation at 0 K which turns out to be equal to 19.5 μ_B, i.e. very near to the value of 20 μ_B of the non substituted ferrite. From the obtained $M_s(0)$ value, with the same procedure described above for the Sc substituted compounds, the probability of entrance of In^{3+} ions in the spin up and spin down sublattices was deduced and utilised for calculating the expected saturation magnetisation at 0 K as a function of x in the hypothesis of axial magnetic order (see Fig. 9). It can be seen that for $x = 2$ the experimental value markedly deviates from the calculated one; the observed difference corresponds to a mean angle of deviation of the Fe^{3+} magnetic moments from the c-axis orientation of $16 \pm 2°$.

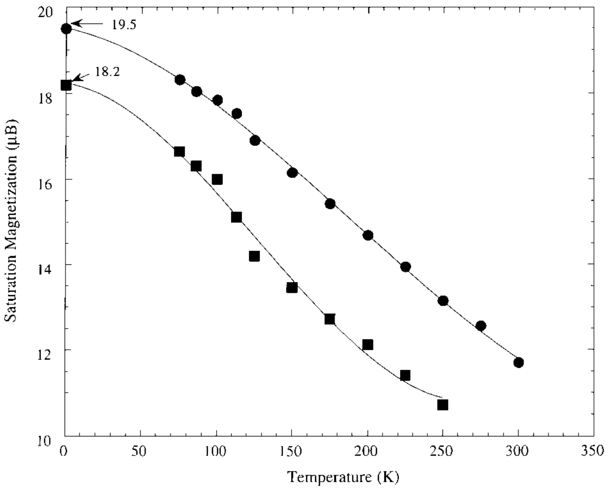

Figure 10 Temperature dependence of the saturation magnetisation (M_s) in Bohr magnetons per unit formula for the $PbFe_{12-x}In_xO_{19}$ compounds; (●) $x = 1$; (■) $x = 2$.

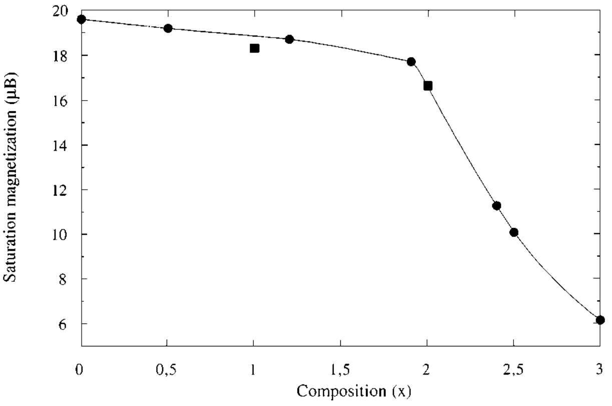

Figure 11 Saturation magnetisation at 77 K vs. x for $PbFe_{12-x}In_xO_{19}$ compounds (■). The circles (●) denote the values for $BaFe_{12-x}In_xO_{19}$ compounds reported in Ref. [6].

4. Conclusions

The substitution of Fe^{3+} by Sc^{3+} and In^{3+} ions in $PbFe_{12}O_{19}$ ferrite strongly influences the sublattice magnetisation and the magnetic order of the compound. This is evident from the Mössbauer spectra of the substituted samples in which various distinct sextets attributable to Fe^{3+} ions of the sublattice k appears. Changes in the quadrupole splitting are induced by the formation of angles between the magnetic moments of the non substituted Fe^{3+} ions and the hexagonal c-axis. The appearance of angled spin structures are also evident from the $M_s(T)$ curves. The canting angles and the temperatures at which the onset of the angled spin structures takes place differs from that observed in Sc and In substituted barium ferrite.

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