

Magnetic and Mössbauer investigation of $\text{PbFe}_{12-x}\text{Ga}_x\text{O}_{19}$ hexagonal ferrites

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Magnetic and Mössbauer measurements have been performed on polycrystalline samples of Ga substituted M-type hexagonal ferrites having compositions $\text{PbFe}_{12-x}\text{Ga}_x\text{O}_{19}$ ($0 < x < 11$). The saturation magnetisation (σ_S) at 0 K falls with increasing x , from $20 \mu_B$ for $x = 0$ to $4.32 \mu_B$ for $x = 6$. The Curie temperature tends to zero at $x \approx 9$, indicating that the compounds with $x > 9$ are paramagnetic at all temperatures. The magnetic moments of the non substituted Fe^{3+} ions in the spin-up predominant sublattice do not have the same temperature dependence, because of the presence of non magnetic Ga^{3+} ions in the neighbouring lattice sites. For $x < 3$, the Mössbauer data show that there is no significant deviation from collinear magnetic order. The decrease of $\sigma_S(0)$ for $x < 3$ agrees with the collinear model and the distribution of gallium in all the five available sublattices. At $x > 3$, the faster decline of the saturation magnetisation can be attributed to the onset of non collinear magnetic order. © 2002 Kluwer Academic Publishers

1. Introduction

The effects of the substitution of iron ions by magnetic and non magnetic ions in hexagonal ferrites continue to attract attention [1, 2]. Considerable effort has been devoted to compare the intrinsic magnetic properties of substituted M-type Pb-hexaferrites with the better known properties of the analogous Ba or Sr compounds. Interest arises from the fact that the heavy divalent cations (Ba^{2+} , Sr^{2+} , Pb^{2+}) play an important role in the M-type structure by influencing the dynamics and the local symmetry of the neighbouring Fe^{3+} ions. Pb^{2+} has a ionic radius between those of Ba^{2+} and Sr^{2+} but, differently from Ba^{2+} and Sr^{2+} that both have electronic configurations typical of alkaline earth metals (p^6), has two electrons in the $6s^2$ shell which can make significant covalent contributions to the bondings with neighbouring ions. Differences in the parameters of Mössbauer spectra and in the substitution probability of Fe^{3+} in the various sublattices have been found for Al substituted Ba and Pb ferrites [3]. Moreover, the interest in the basic properties of Pb hexaferrites is linked to research on the preparation of films of Pb based hexagonal ferrites which need lower growth temperatures than ferrites containing Ba or Sr [4]. Recently, we have also considered the substitution of iron with In and Sc [5].

Though the Ga substituted M-type ferrite was one of the first hexaferrites studied by Mössbauer spec-

troscopy [6], its magnetic order is still an open question. Marisko *et al.* [7] reported the results of magnetic measurements on single crystals of $\text{PbFe}_{12-x}\text{Ga}_x\text{O}_{19}$ for $x < 8$ evidencing, for some compositions, a peculiar phenomenon of anisotropy of the Curie temperature (T_C) and hypothesising deviations from the collinear magnetic order for $x > 3$. However, more experimental data are needed to understand the spin configuration in the highly substituted ferrite.

In this paper the results of Mössbauer and magnetic measurements on polycrystalline samples of $\text{PbFe}_{12-x}\text{Ga}_x\text{O}_{19}$ ($0 < x \leq 11$), prepared by standard ceramic method, are reported and discussed. From the Mössbauer spectra at $T > T_C$ the determination of the substitution probability of iron in the pseudo-hexahedral sublattice b has been made with greater accuracy than in early works. The data obtained on the magnetic order and on the cationic distribution allow a better understanding of the dependence of the saturation magnetisation on substitution.

2. Experimental

Polycrystalline samples of $\text{PbFe}_{12-x}\text{Ga}_x\text{O}_{19}$ ($0 < x \leq 11$) were prepared by the ceramic method. Because of the volatility of Pb, particular attention was devoted to the choice of the presintering temperature to obtain homogeneous M-type hexagonal phase.

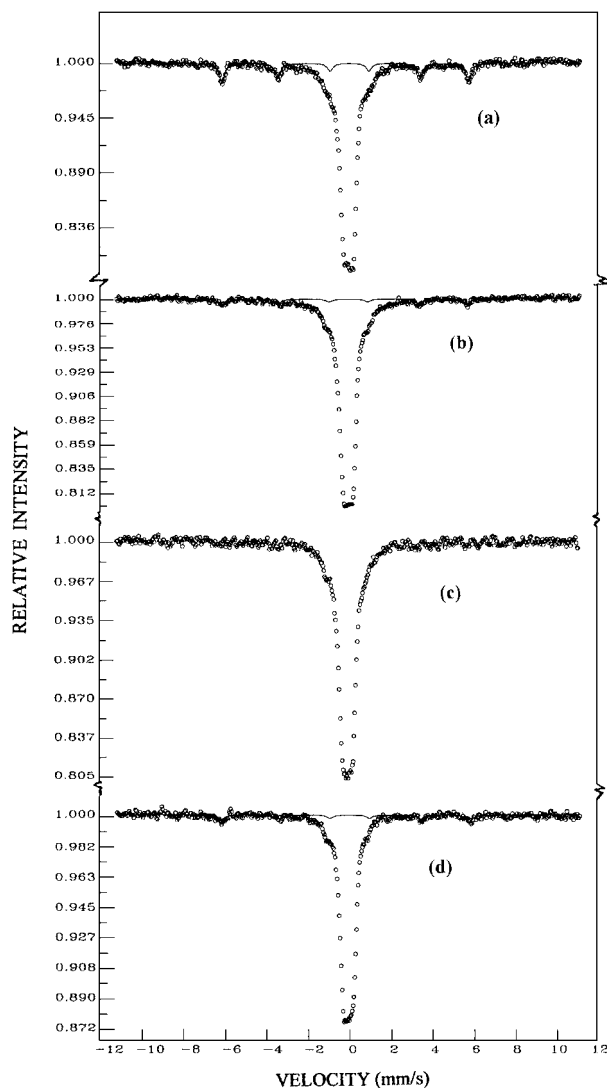


Figure 1 Fe^{57} -Mössbauer spectra measured at $T = 753^\circ C$ for samples with stoichiometric composition $PbFe_{12}O_{19}$ heated at: (a) $T = 850$; (b) $T = 875$; (c) $T = 900$; and (d) $T = 925^\circ C$.

Fig. 1 shows the Mössbauer spectra of $PbFe_{12}O_{19}$ samples prepared at various presintering temperatures, measured at $T \approx 480^\circ C$, i.e., at a temperature above the T_C of the hexagonal phase but below that of Fe_2O_3 . Beside the central part of the spectrum, resulting from the hexagonal phase in the paramagnetic state, a sextet typical of Fe_2O_3 appears in the spectra of the samples heated at 850, 875, 925 $^\circ C$, with a relative intensity which depends on the heating temperature. Often, traces of the Fe_2O_3 phase are not detected by X-ray diffraction because of the small dimensions of the particles. The analysis performed by Mössbauer spectroscopy was used to choose the correct presintering temperature. All the samples of $PbFe_{12-x}Ga_xO_{19}$ were prepared using high purity (>99.99%) Fe_2O_3 , Ga_2O_3 and PbO powders. The raw materials were mixed in isopropanol in a ball mill. After the material was dried, disks were pressed and then presintered at $900^\circ C$ for 2 hours. The presintered disks were pulverised and milled as before, pressed again and sintered at $1000^\circ C$ for 2 hours.

The homogeneity of the compounds obtained was checked both by X-ray and Mössbauer analysis. X-ray spectra of all the series are typical of M-type hexaferrite.

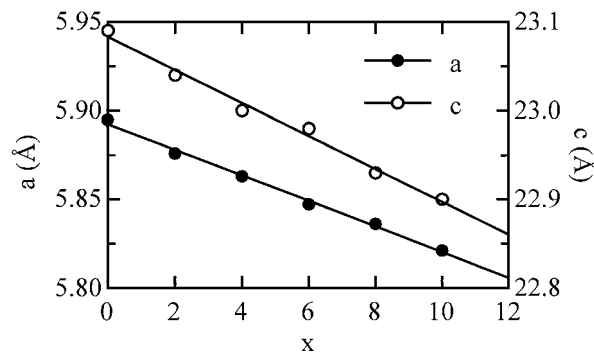


Figure 2 The variation of the a (—●—) and c (—○—) lattice constants as a function of composition of the $PbFe_{12-x}Ga_xO_{19}$ (for $x=0$ see Ref. [8]).

In Fig. 2 the variation of the a and c lattice constants of the hexagonal unit cell for $PbFe_{12-x}Ga_xO_{19}$ is reported. The temperature dependence of the DC susceptibility at low magnetic field was measured for all the samples with $x < 6$. A single and well-defined knee was detected at the Curie temperature.

The saturation magnetisation (σ_S), in the range 77–300 K and the coercive field (H_C) at room temperature were measured with an Oxford 3001 vibrating sample magnetometer, working at H_{max} of 16 kOe.

The Mössbauer absorption spectra of the Fe^{57} 14.4 keV γ -radiation were recorded using a Co^{57} source in a Rh matrix at RT with the absorber held at fixed temperatures ranging from 77 to 800 K.

3. Results and discussion

The Curie temperatures for the samples $PbFe_{12-x}Ga_xO_{19}$ with $x \leq 6$ have been determined both by measuring the temperature dependence of the width of the Mössbauer absorption band near T_C , and of the transmission intensity of the Mössbauer radiation at zero velocity. These were compared with measurements performed on $SrFe_{12-x}Ga_xO_{19}$ ($0 < x < 8$). The T_C values for the two series of compounds show a similar decrease with increasing x (see Fig. 3). These data also agree with those reported by Marisko *et al.* [7] for $PbFe_{12-x}Ga_xO_{19}$ single

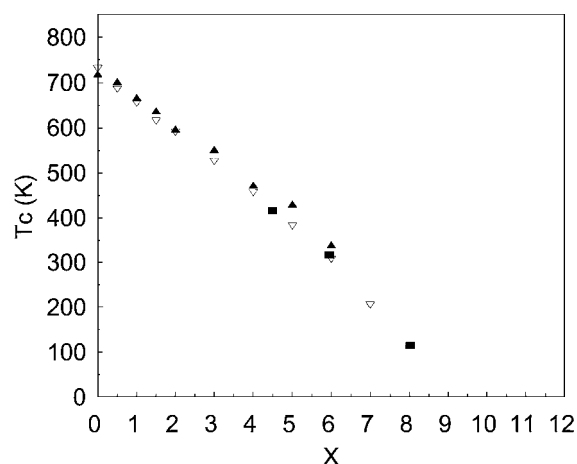


Figure 3 Curie temperatures for $PbFe_{12-x}Ga_xO_{19}$ (\blacktriangle) and $SrFe_{12-x}Ga_xO_{19}$ (∇) hexaferrites. The squares (\blacksquare) denote the mean values for $PbFe_{12-x}Ga_xO_{19}$ reported in Ref. [7].

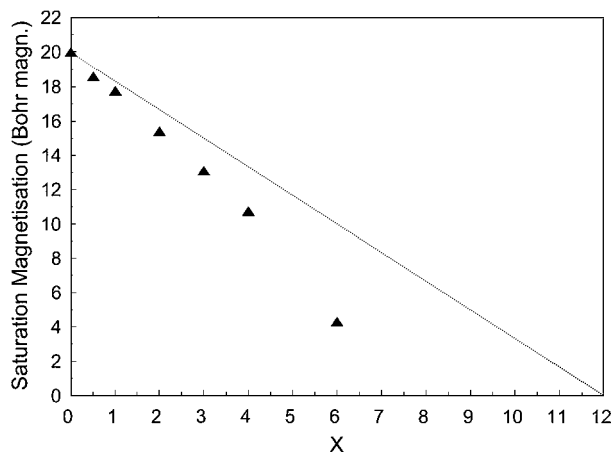


Figure 4 Saturation magnetisation in Bohr magnetons per unit formula for $\text{PbFe}_{12-x}\text{Ga}_x\text{O}_{19}$ hexaferrites at $T = 0$ K (▲). The line denotes the calculated values in the hypothesis of axial magnetic order and equiprobable distribution of Ga^{3+} ions among all the available lattice sites.

crystals with $x = 4.49, 5.94$ and 8.02 , taking the mean values of the T_C measured parallel and perpendicular to the c -axis. The $T_C(x)$ curve tends to zero value for $x \approx 9$, indicating that the compounds $\text{PbFe}_{12-x}\text{Ga}_x\text{O}_{19}$ for $x \geq 9$ are always paramagnetic.

For the samples with $x < 6$ the saturation magnetisation has been measured between 77 and 300 K; the values obtained display a monotonic dependence on T and allow a reliable extrapolation to lower temperatures to determine saturation magnetisation at 0 K. The $\sigma_S(0)$ value falls rapidly from $20 \mu_B$ for $x = 0$ to $4.32 \mu_B$ for $x = 6$ (see Fig. 4).

In the M-type ferrite, the 12 iron ions per formula unit are distributed among five sublattices: six in the octahedral sublattice k (spin up), one in the octahedral sublattice a (spin up), one in the pseudo-hexahedral sublattice b (spin up), two in the tetrahedral sublattice fIV (spin down), and two in the octahedral sublattice fVI (spin down). The sublattice b is indicated as pseudo-hexahedral because the cation is displaced from the symmetry plane of the coordination trigonal bipyramid, and it plays the main role in determining the magnetic anisotropy properties of the M-type ferrites.

Mössbauer spectroscopy is very effective for determining the substitution of iron in the b lattice sites. In fact, in the spectra measured at $T > T_C$, the large quadrupole splitting of the b sublattice makes the corresponding doublet clearly distinguishable from the rest of the spectrum. Accurate measurements of the Mössbauer spectra at $T > T_C$ were performed on all the samples. The spectra were interpreted as the superposition of five quadrupole doublets corresponding to the five iron sublattices of the M-structure. The same procedure described in Ref. [3] was adopted to fix the starting parameters required to fit the spectra. The spectrum of the sample with $x = 10$, measured at $T = 295$ K, is shown in Fig. 5, with the doublet resulting from the sublattice b evidenced. In Fig. 6, the ratio of the areas submitted by the b doublet to the total area of the spectrum is compared with the values calculated presuming various hypotheses on the order of substitution. It was assumed that the Debye-Waller factors are not affected by the substitution. The constancy of the ratio I_b/I_{total}

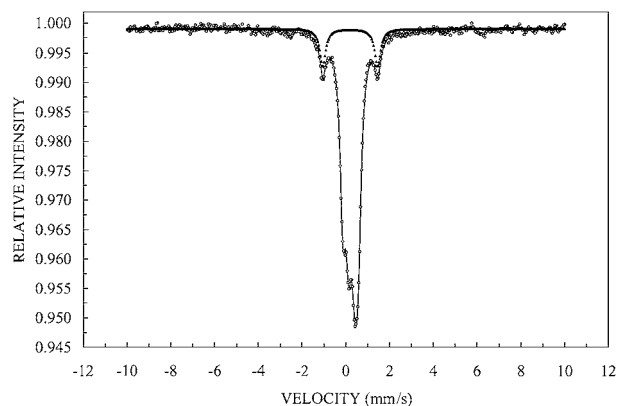


Figure 5 Fe^{57} -Mössbauer spectrum for $\text{PbFe}_{12-x}\text{Ga}_x\text{O}_{19}$ ($x = 10$) compound at $T = 295$ K. Experimental points (○ ○ ○); fitted spectrum (—) as a sum of five doublets. The doublet of the b sublattice is evidenced (▲▲▲).

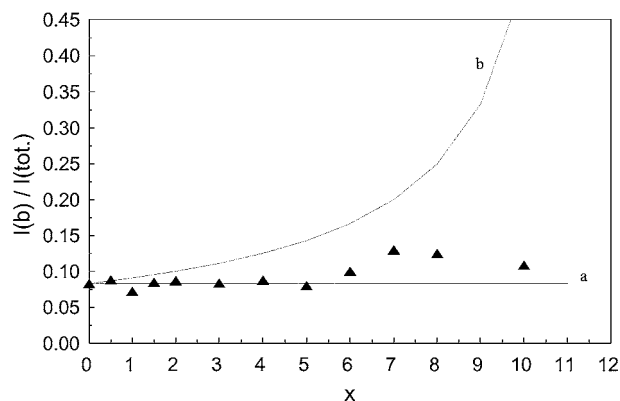


Figure 6 Dependence on x of the ratio between the area submitted by the doublet b and the total area of the Mössbauer spectrum of $\text{PbFe}_{12-x}\text{Ga}_x\text{O}_{19}$ compounds above T_C (▲). The lines denote the expected values in the hypotheses of a statistical distribution of gallium in all the lattice sites (a) and with the exclusion of the sublattice b (b). The data are normalised to the value determined for $x = 0$.

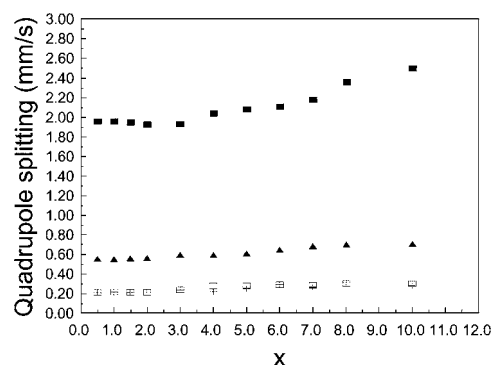


Figure 7 Quadrupole splitting for Fe^{57} nuclei in the various sublattices of $\text{PbFe}_{12-x}\text{Ga}_x\text{O}_{19}$ compounds above T_C . Sublattices k (▲); e (■); fVI (□); fIV (+). It is zero at all values of x for the a sublattice, within experimental accuracy.

upon x indicates that up to $x \approx 5$ the Ga^{3+} ions enter the b lattice sites with nearly the same probability as the remaining sublattices. Some scatter of the experimental points at higher x indicates a small decrease of the substitution probability in the b sublattice.

The quadrupole splittings (QS) for Fe^{57} nuclei in the various sublattices at $T = 743$ K are shown in Fig. 7, and it can be seen that they change only slightly with composition.

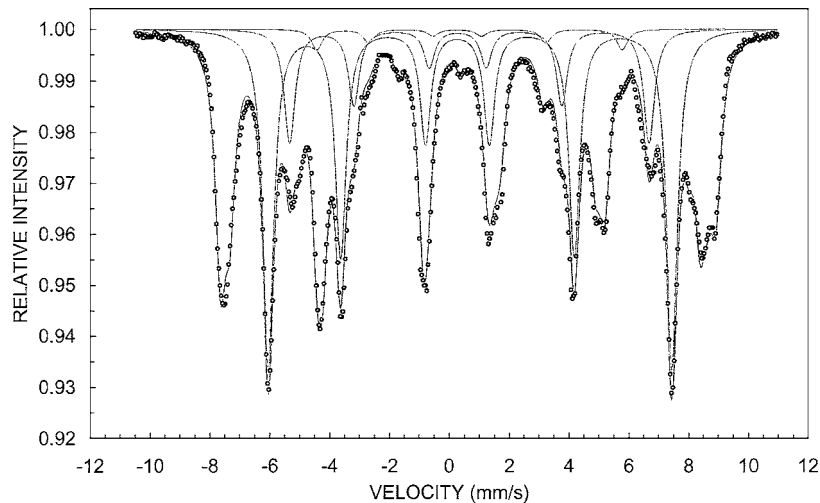


Figure 8 ^{57}Fe -Mössbauer spectrum for $\text{PbFe}_{12-x}\text{Ga}_x\text{O}_{19}$ ($x=0.5$) compound at $T=295$ K. Experimental points ($\circ \circ \circ$); spectrum fitted as superposition of five sextets (—). For better clarity only the subspectra of the sublattices k (- - -) are traced.

The substitution of the Fe^{3+} by Ga^{3+} strongly influences the magnetisation of the sublattice k . In the Mössbauer spectra at $T < T_C$ the nuclear Zeeman sextet of the non substituted Fe^{3+} in the k sublattice sites splits into different sextets (k' , k'' , ...) which correspond to lower hyperfine magnetic fields (H_{hf}). This is evident in Fig. 8 even at low x ; for $\text{PbFe}_{12-x}\text{Ga}_x\text{O}_{19}$ ($x=0.5$) at 295 K, the k' and k'' sextets appear beside the intense k sextet. As x increases, other sextets appear with higher relative intensities. Their hyperfine magnetic fields have a different temperature dependence because of the different temperature behaviour of the magnetic moments of the non substituted iron in k sublattice. This phenomenon has also been seen in In and Sc substituted ferrites [5] but not in those with Al [3, 6]. The appearance of the k' , k'' , k''' , ..., sextets, is interpreted as a consequence of the non magnetic ions present in the f sublattices which are magnetically strongly coupled with the sublattice k . The iron ions of the k sublattice that have lost part of the superexchange interaction with the ions in the f sublattice shows a more rapid decrease of their magnetic moment with increasing temperature.

To verify the onset of angled spin configurations, particular attention was paid to the determination of the quadrupole splittings which, below T_C , depend on the angle between the Fe^{3+} magnetic moments and the axis of the electric field gradient. Unfortunately, the multiple k sublattice sextets make the spectra very complex for high values of x , thus, their univocal interpretation was possible only for $x \leq 2$. In Table I, the quadrupole

splitting of the k and k' sextets, deduced from the room temperature spectra of the samples with $x=0, 0.5, 1, 1.5, 2$ are reported. The ratio between the QS below and above T_C indicates, within experimental error, that no deviation from axial magnetic ordering takes place.

The relative peak intensities of the different sublattices below T_C agree with those measured above T_C . This indicates that the gallium substitutes iron with equal probability in all the lattice sites.

Between $x=0$ and 2 the experimental values of the saturation magnetisation at 0 K were compared with those calculated assuming the above hypothesis for the distribution of gallium (Fig. 4). The experimental values are seen to decrease a little more rapidly with x . Better agreement with the calculated values of $\sigma_S(0)$ can be reached by admitting a slightly greater probability of Ga substitution in the spin-up sublattices. This cannot be excluded because it implies a very small variation in ratio of the relative area of the spin-up and spin-down subspectra, beyond our experimental accuracy.

The large decrease of $\sigma_S(0)$ for $x \geq 3$ may be a result of the onset of non collinear magnetic order. Angled spin ordering at $x > 3$ has been used by Marisko *et al.* [7] to explain the results of magnetic measurements on $\text{PbFe}_{12-x}\text{Ga}_x\text{O}_{19}$ single crystals.

4. Conclusions

The Mössbauer spectra of $\text{PbFe}_{12-x}\text{Ga}_x\text{O}_{19}$ with $x < 3$, below T_C show that the substitution of iron by gallium strongly perturbs the temperature dependence of the magnetisation of the predominant k sublattice. The Curie temperature tends to zero at $x \approx 9$, suggesting that the compounds with $x > 9$ are paramagnetic at all temperatures.

The Mössbauer spectra indicate that up to $x=2$ the spin order remains collinear. The relative line intensities in the Mössbauer spectra indicate that the Ga^{3+} ions distribute themselves with nearly equal probability in all the available sublattices. The dependence of $\sigma_S(0)$ on x , in the interval $0 < x < 3$, suggests a slight preference for the spin-up sublattices. The more rapid decrease of $\sigma_S(0)$ for values of x above 3 could be attributed to the onset of non collinear magnetic order.

TABLE I Quadrupole splitting of the Fe^{57} nuclei in the k lattice sites

$\text{PbFe}_{12-x}\text{Ga}_x\text{O}_{19}$	Sextet	ΔQ (mms $^{-1}$)
$x=0$	k	0.042 ± 0.01
	k'	—
$x=0.5$	k	0.042 ± 0.01
	k'	0.041 ± 0.02
$x=1$	k	0.042 ± 0.01
	k'	0.043 ± 0.02
$x=1.5$	k	0.043 ± 0.02
	k'	0.044 ± 0.02
$x=2$	k	0.044 ± 0.02
	k'	0.045 ± 0.02

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