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^{57}Fe Emission Mössbauer Study on $Gd_3Ga_5O_{12}$ implanted with dilute ^{57}Mn

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Abstract ^{57}Fe emission Mössbauer spectroscopy has been applied to study the lattice location and properties of Fe in gadolinium gallium garnet $Gd_3Ga_5O_{12}$ (GGG) single crystals in the temperature interval 300 – 563 K within the extremely dilute ($<10^{-4}$ at.%) regime following the implantation of ^{57}Mn ($T_{1/2}$ = 1.5 min.) at ISOLDE/CERN. These results are compared with earlier Mössbauer spectroscopy study of Fe-doped gadolinium gallium

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garnet $Gd_3Ga_5O_{12}$(GGG), with implantation fluences between $8{\times}10^{15}$ and $6{\times}10^{16}$ atoms cm^{-2}. Three Fe components are observed in the emission Mössbauer spectra: (i) high spin Fe^{2+} located at damage sites due to the implantation process, (ii) high spin Fe^{3+} at substitutional tetrahedral Ga sites, and (iii) interstitial Fe, probably due to the recoil imparted on the daughter ^{57*}Fe nucleus in the β^- decay of ^{57}Mn. In contrast to high fluence ^{57}Fe implantation studies the Fe^{3+} ions are found to prefer the tetrahedral Ga site over the octahedral Ga site. No annealing stages are evident in the temperature range investigated. Despite the very low concentration, high-spin Fe^{3+} shows fast spin relaxation, presumably due to an indirect interaction between nearby gadolinium atoms.

Keywords Gadolinium gallium garnet ($Gd_3Ga_5O_{12}$) · ^{57}Mn implantation · Mössbauer emission spectroscopy · Fe sites

1 Introduction

Iron doping of gadolinium gallium garnet $Gd_3Ga_5O_{12}$ (GGG) has been shown to enhance the magnetocaloric effects of the material [1, 2]. It has been suggested that this is due to Fe^{3+} ions mediating exchange interactions between Gd ions, but no microscopic investigation of this effect has been performed. In this study we investigate the Fe doping by ion-implantation in the truly dilute ($<10^{-4}$ at%) regime utilising ^{57}Fe emission Mössbauer spectroscopy (eMS).

The cubic structure of the gadolinium gallium garnet is illustrated in Fig. 1. It is formed as $[C]_3([A]_2[D]_3)O_{12}$ with a unit cell comprising eight sublattices. Gd ions as [C] ions are located at dodecahedral (24c) sites, while Ga ions as [A] and [D] ions occupy octahedral (16a) and tetrahedral (24d) sites, respectively.

Earlier Mössbauer Spectroscopy study of Fe-doped GGG [4], with implantation fluences between $8{\times}10^{15}$ to $6{\times}10^{16}$ atoms cm^{-2} and after annealing up to 600°C, found the implanted Fe^{3+} substituted gallium atoms both at the octahedral and the tetrahedral positions, with the octahedral site preferred at the highest fluences. Fe^{3+} in the octahedral site was characterized by an isomer shift of $\delta = 0.35$ mm/s and a quadrupole splitting of $\Delta E_Q = 0.37$ mm/s and the corresponding parameters in the tetrahedral site were $\delta = 0.16$ mm/s and $\Delta E_Q = 1.03$ mm/s.

2 Experimental

Radioactive beams of $^{57}Mn^+$ ($T_{1/2} = 85.4$ s) were produced at the ISOLDE facility at CERN by 1.4 GeV proton-induced fission in a heated UC_2 target and elemental selective laser multi-photon ionization [5]. After acceleration to 50 keV and magnetic mass separation, pure beams of $\sim 2{\times}10^8$ $^{57}Mn^+$/s were obtained.

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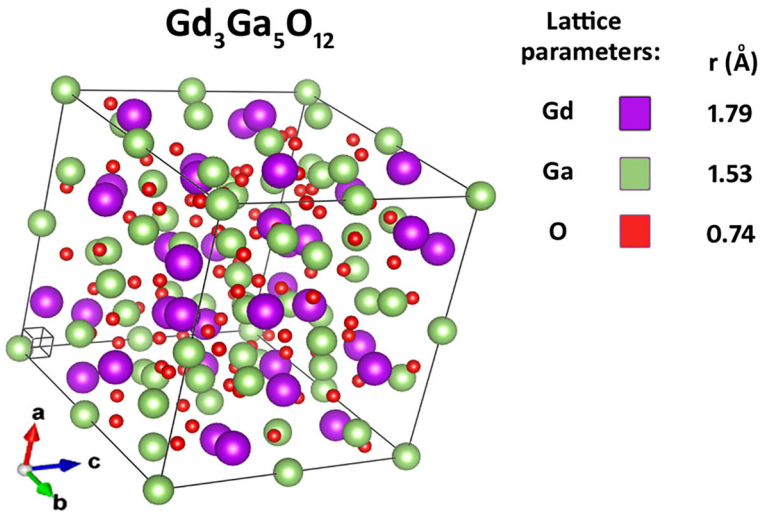

Fig. 1 Lattice structure of $Gd_3Ga_5O_{12}$ garnet showing the distribution of the Gd, Ga and O ions [3]

Dilute $^{57}Mn^{+}$ ions were implanted into $Gd_3Ga_5O_{12}$ single crystal samples at an incident angle of $\theta_I = 30°$ relative to the sample surface normal. Emission Mössbauer spectra (eMS) were measured on-line on the 14.4 keV Mössbauer state of the daughter $^{57*}Fe$ ($T_{1/2} = 98$ ns) with an acetone gas-filled parallel-plate avalanche resonance detector, equipped with stainless steel electrode enriched in ^{57}Fe. The experimental line-width of the detector and setup is described with a Voigt profile with Lorentzian FWHM broadening of $\Gamma_D = 0.34$ mm/s and Gaussian broadening of $\sigma_D = 0.08$ mm/s. The detector was mounted outside the implantation chamber on a conventional constant-acceleration drive system at 90° relative to the beam direction (60° relative to the normal to the crystal surface). The spectra were recorded continuously for 10 min. from the start of the implantation. The maximum implanted fluence was ($\sim 2\times10^{12}$ $^{57}Mn/cm^2$) corresponding to a local concentration of less than 10^{-4} at.%. The samples were measured and held at the different temperatures by a lamp heating the sample backside. Velocities and isomer shifts are given relative to the centre of the α-Fe spectrum at room temperature.

3 Results

The ^{57}Fe eMS obtained after implantation of ^{57}Mn into a $Gd_3Ga_5O_{12}$ single crystal at sample temperatures between 303 K and 563 K, are presented in Fig. 2.

The overall shape of the spectra is a convolution of two or more doublets with no sign of any magnetically-split sextet component. A fitting strategy was adopted in which three doublet components with Voigt line-shapes were applied (Fig. 2) to simultaneously fit the spectra over the entire temperature range of measurements, assuming temperature independent line-widths. The resulting hyperfine parameters are gathered in Fig. 2, with corresponding site assignments as discussed below and the relative areas in Fig. 3.

The isomer shift data for all three doublets followed the second order Doppler (SOD) shift with temperature. The broad lines associated with DB1 suggest Fe in highly distorted

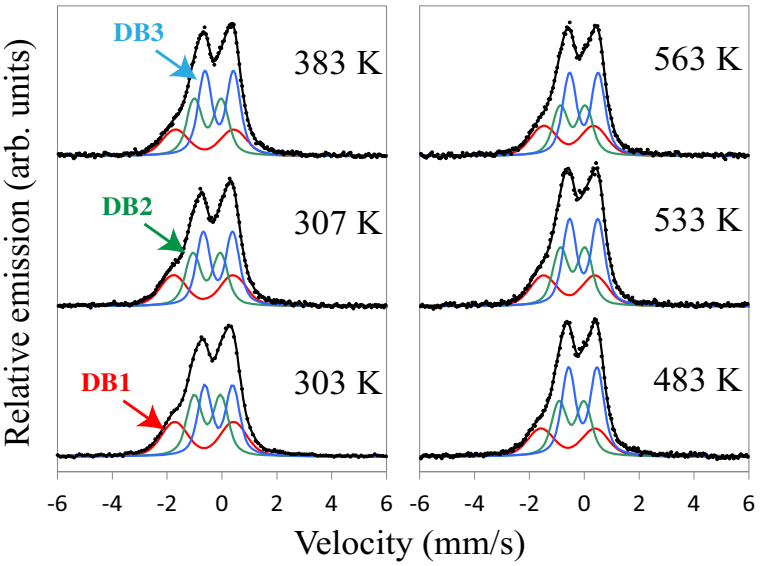

Fig. 2 ^{57}Fe eMS spectra obtained after implantation of ^{57}Mn into GGG crystals held at the temperatures indicated. The solid lines show the fitting components as labelled and their sum

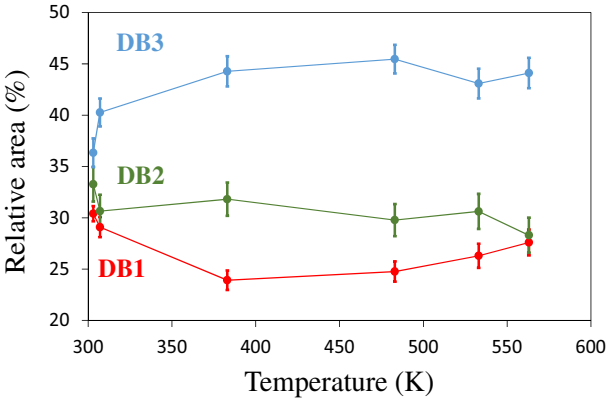

Fig. 3 Relative areas of the spectral components as a function of temperature

lattice environment, due to extended lattice damage resulting from the implantation process. The hyperfine parameters are consistent with high-spin Fe^{2+} in amorphous zones as observed in several ion implanted insulators [6].

4 Discussion

The isomer shift and negligible temperature dependence of the quadrupole splitting (Table 1) of DB3 are consistent with an assignment as originating from high-spin Fe^{3+}. In order to interpret this component further, we discuss it in comparison with results

Table 1 Summary of hyperfine parameters. δ_{RT} is the isomer shift at room temperature, $\Delta E_{Q,RT}$ the quadropole splitting at room temperature, $d\Delta E_Q/dT$ the temperature dependence of the quadrupole splitting throughout the temperature range and σ the Gaussian broadening of the spectral lines additional to the experimental line width of the detector

Component	Site assignment	δ_{RT} (mm/s)	$\Delta E_{Q,RT}$ (mm/s)	$d\Delta E_Q/dT$ (mm/(s.K))	σ (mm/s)
DB1	Fe^{2+} damage	0.65(1)	2.15(4)	-120(20)×10^{-5}	0.33(1)
DB2	Interstitial Fe	0.53(1)	0.97(1)	-34(5)×10^{-5}	0.19(1)
DB3	Fe^{3+} on Ga_T sites	0.12(1)	1.02(1)	-3(4)×10^{-5}	0.17(1)

obtained on ^{57}Fe implanted samples in the fluence range from 8×10^{15} – 6×10^{16} cm^{-2} of Szucs et al., [4]. Their spectra, after annealing at $T \geq 600$°C, showed three components: "Prec" assigned to Fe in Fe^{3+} containing precipitates, "T" assigned to Fe^{3+} on tetrahedral Ga sites and "O" assigned to Fe^{3+} on octahedral Ga sites [4]. The hyperfine parameters of the "T" component ($\delta_{RT} = 0.16$ mm/s, $\Delta E_{Q,RT} = 1.03$ mm/s) correspond well with the DB3 component observed here (see Table 1). The temperature dependence of the quadrupole splitting of the DB3 component likewise supports this identification, since it exhibits an insignificant variation (see Table 1), as is expected for high-spin Fe^{3+}.

DB2 is characterized by a relatively small line-width suggesting a more regular crystalline site (not amorphous site). The hyperfine parameters of DB2 in our study are different from the components observed in higher fluence ^{57}Fe implanted samples [4], in particular, the isomer shift observed here ($\delta_{RT} = 0.53(1)$ mm/s) is inconsistent with Fe^{3+} on octahedral Ga sites ($\delta_{RT} = 0.35$ mm/s [4]). A tentative assignment of DB2 could therefore be interstitial Fe, either due to implantation directly on interstitial sites or due to the recoil ($\langle E_R \rangle = 40$ eV, $E_{R,Max} = 93$ eV) imparted on the ^{57}Fe daughter nucleus in the β^-decay of ^{57}Mn resulting in a relocation of the Fe to interstitial sites. In comparison, the calculated threshold displacement energy for $Gd_3Ga_5O_{12}$ has been estimated as ~ 56 eV [7], far less than the maximum recoil energy and the assignment of the DB2 originating from interstitial Fe is the most likely. From the present experimental data it is not possible to determine the ionic state of the interstitial Fe.

In the super-dilute regime reported here, we thus observe that the implanted Fe^{3+} is found to occupy only tetrahedral Ga sites and there is no evidence of octahedral substitution. This contrasts the observations of Szucs et al. [4], where the octahedral occupancy could be a consequence of the relatively high iron concentration.

It is of interest to note, that despite the extreme dilution used, sextet-like spectral components due to slow paramagnetic relaxation of Fe^{3+} are not observed as in similar eMS experiments in other oxides [8–11]. Instead high-spin Fe^{3+} (Fe^{3+} on Ga_T sites, DB3) show fast ($>10^{10}$ Hz) spin relaxation and is observed as a doublet. This indicate that there is an interaction between Fe and Gd ions which would result in fast spin-spin relaxations. This is in agreement with the observation of McMichael et al., [12] who observed enhanced magnetocaloric effect proposed to originate from Fe^{3+} mediating exchange interaction between Gd^{3+} ions.

Within the temperature range of this study, definite signs of an annealing stage are not observed which, for example, would be noted as a prompt change in the area fractions (Fig. 3), suggesting that annealing at higher temperature is needed to incorporate all ions on regular lattice sites.

5 Conclusion

We have by means of emission Mössbauer spectroscopy investigated the lattice sites occupied of dilute Fe in $Gd_3Ga_5O_{12}$ in the temperature range from room temperature to 563 K. Dilute ion-implantation results in three components; high spin Fe^{3+} on substitutional Ga_T sites, interstitial Fe, and Fe^{2+} in amorphous zones. No annealing stage between RT and $\sim$ 560 K is observed. High spin Fe^{3+} in this material shows fast spin relaxation despite the very low concentration ($<10^{-4}$ at.%) utilized in this study, presumably due to exchange interaction with Gd^{3+}.

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