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Mössbauer study of ion-implanted $\text{Co}_x\text{Ga}_{1-x}$ alloys

I Dézsi†||, I Szűcs†, Cs Fetzter†, G Langouche‡, H Pattyn‡ and W Keune§

† MTA-KFKI Research Institute for Particle and Nuclear Physics, H-1525 Budapest 114, PO Box 49, Hungary

‡ IKS, Katholieke Universiteit Leuven, B-3001 Leuven, Belgium

§ Laboratorium für Angewandte Physik, Gerhard Mercator Universität, D-4100 Duisburg 1, Germany

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Abstract. Mössbauer effect studies of implanted and synthesized $\text{Co}_x\text{Ga}_{1-x}$ alloys are presented. The spectra showed broad lines indicating at least two components corresponding to Co sites in the two sublattices. Ion implantation resulted in an increase of the Co population in antistructure positions. The broad spectral component of ^{57}Fe in the Co sublattice was attributed to electric quadrupole splitting induced by vacancies and antistructure atoms lowering the local symmetry. A new attribution of the Mössbauer parameters to the various atomic configurations is suggested.

1. Introduction

The β -phase alloy form of $\text{Co}_x\text{Ga}_{1-x}$ exists between $x = 0.4$ and $x = 0.65$ and has B2 (CsCl) cubic structure [1]. In several B2 alloys, very high thermal defect concentrations of the order of a few per cent appear [2], especially in nonstoichiometric samples with $x < 0.5$, after quenching from the melting temperature. Antistructure Co atoms are formed for $x > 0.5$ [3–5]. Mössbauer studies showed broadened resonance lines for $(^{57}\text{Co})^{57}\text{Fe}$ sources. For ^{57}Fe absorbers, complex spectra with several spectral components were observed [6–8] and the isomer shift values indicated that iron is located in the Ga sublattice. The spectra for the ^{57}Co source were analysed in terms of a model predicting the relative concentrations of the various local atomic configurations around Co [7]. It was also suggested that the vacancies are only in the Co sublattice. In a recent paper [9] point defects in B2 alloys were studied using perturbed gamma angular correlation. It seemed that it would be of interest to introduce ^{57}Co by ion implantation into these alloys to create defects and possibly observe their effects on the neighbouring Co atoms.

2. Experimental procedure

^{57}Co ions were implanted in the Leuven isotope separator into the alloy samples with $x = 0.48, 0.50, 0.52, 0.54$ with a dose of 5×10^{13} atoms cm^{-2} at 80 keV. The implantation was performed at room temperature. The ingots were prepared by melting in an induction oven in a pure Ar atmosphere, using 5N Co and Ga. The single-B2-phase structure of the alloys was proved by x-ray diffraction. The weight loss of the ingots after

|| Also at: KFKI Research Institute for Material Research.

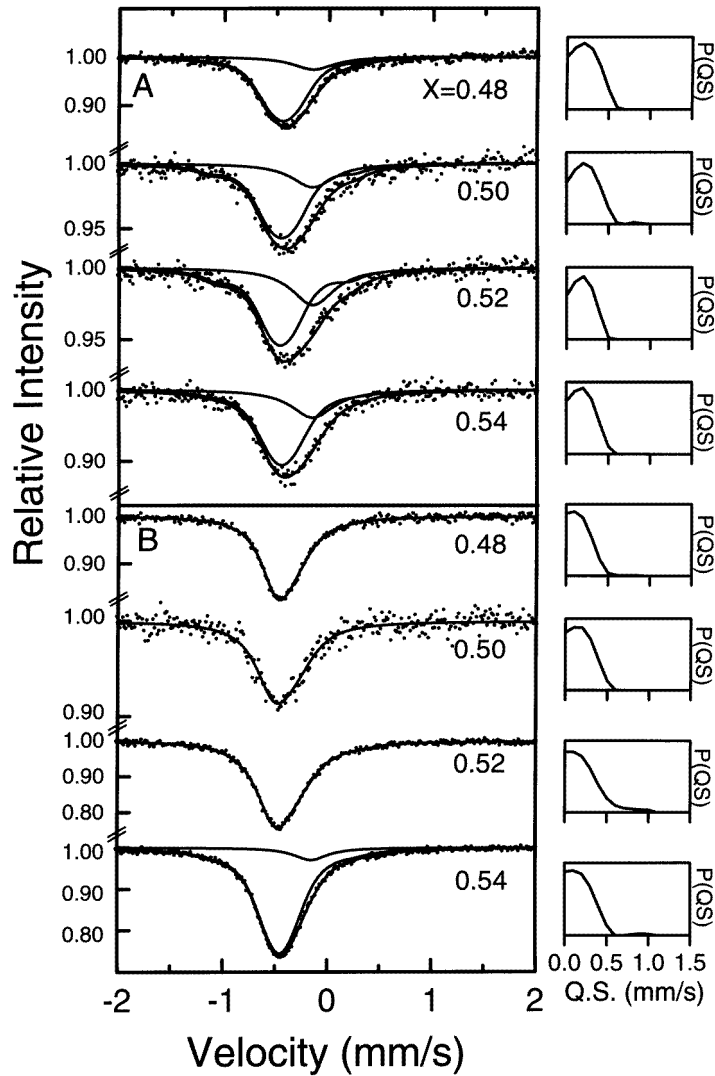


Figure 1. Mössbauer spectra of implanted (A) and annealed (B) samples.

melting was less than 0.1 weight per cent. Quenched and slowly cooled samples were prepared. For implantation, slowly cooled samples were used in order to minimize the vacancy concentration in the target material. The Mössbauer spectra were measured using $\text{Na}_4[\text{Fe}(\text{CN})_6]$ single-line absorbers with 0.5 mg cm^{-1} ^{57}Fe thickness. The measurements were made at room temperature. Thermal annealings of the implanted spectra were made in vacua of 4×10^{-1} Pa and also in an Ar atmosphere at $800 \text{ }^\circ\text{C}$ for 10 minutes. No differences between the spectra of the samples treated in the different atmospheres could be observed. New $\text{Co}_x\text{Ga}_{1-x}$ source samples were also prepared by diffusing ^{57}Co in Ar atmosphere at 4×10^5 Pa and by melting the alloy samples together with ^{57}Co . After melting, the samples were either quenched or slowly cooled ($10 \text{ }^\circ\text{C h}^{-1}$) from $830 \text{ }^\circ\text{C}$. Loss of Ga in the closed quartz ampoules was excluded. The alloy pieces were crushed, and the powder obtained

Table 1. The Mössbauer parameters of the implanted (A, B) and newly synthesized (C, D) $\text{Co}_x\text{Ga}_{1-x}$ samples. ((I.S.) relative to $\alpha\text{-Fe}$.)

Samples	Quadrupole-split component				Singlet	
	(I.S.) (mm s ⁻¹)	(Q.S.) (mm s ⁻¹)	σ (mm s ⁻¹)	Relative intensity (%)	I.S. (mm s ⁻¹)	Relative intensity (%)
A (as implemented)						
$\text{Co}_{48}\text{Ga}_{52}$	-0.43(1)	0.24(1)	0.22(3)	82(8)	-0.15	18(2)
$\text{Co}_{50}\text{Ga}_{50}$	-0.44(1)	0.32(2)	0.36(3)	76(8)	-0.15	24(2)
$\text{Co}_{52}\text{Ga}_{48}$	-0.45(1)	0.32(2)	0.38(2)	68(7)	-0.15	32(3)
$\text{Co}_{54}\text{Ga}_{46}$	-0.44(1)	0.22(2)	0.23(5)	72(7)	-0.15	28(3)
B (annealed)						
$\text{Co}_{48}\text{Ga}_{52}$	-0.42(3)	0.18(1)	0.18(1)	100(1)		
$\text{Co}_{50}\text{Ga}_{50}$	-0.44(2)	0.19(3)	0.14(2)	100(1)		
$\text{Co}_{52}\text{Ga}_{48}$	-0.42(4)	0.26(1)	0.27(1)	100(1)		
$\text{Co}_{54}\text{Ga}_{46}$	-0.45(1)	0.23(1)	0.27(1)	91(1)	-0.15	9(1)
C (slowly cooled)						
$\text{Co}_{45}\text{Ga}_{55}$	-0.44(2)	0.194(4)	0.160(9)	100(1)		
$\text{Co}_{50}\text{Ga}_{50}$	-0.416(1)	0.188(5)	0.125(7)	100(1)		
$\text{Co}_{54}\text{Ga}_{46}$	-0.445(2)	0.221(4)	0.242(8)	92(2)	-0.15	8(2)
$\text{Co}_{58}\text{Ga}_{42}$	-0.44(1)	0.281(3)	0.310(5)	86(3)	-0.15	14(3)
D (quenched)						
$\text{Co}_{46}\text{Ga}_{54}$	-0.435(8)	0.200(4)	0.154(4)	100(1)		
$\text{Co}_{50}\text{Ga}_{50}$	-0.43(2)	0.247(5)	0.24(1)	100(1)		
$\text{Co}_{58}\text{Ga}_{42}$	-0.445(7)	0.393(5)	0.393(6)	92(5)	-0.15	8(5)

was uniformly spread and fixed on a spot of 8 mm diameter in the sample holder. The measurements were made by using a conventional constant-acceleration spectrometer. The analyses of the Mössbauer spectra were performed by using a program allowing distributions in the hyperfine interaction parameters. This program calculates first theoretical spectra for the different hyperfine interactions, including electric quadrupole interaction. The full static Hamiltonian for the nuclear states is used. The isomer shift is set to zero and the spectra are normalized to unit area. In this way a set of parameter points was obtained. The cubic spline method is used to calculate a smooth curve going through the points of the set. The spline coefficients obtained are stored in the same file as the spectra. In order to fit the experimental spectra, these spectra are read in and corrected for the differences in velocity scale and isomer shifts. The corrected spectra are fitted to the experimental ones and the fitting procedure gave the relative intensities of the subspectra and the parameter distribution curves.

3. Results

The spectra of the as-implanted samples are shown in figure 1(A). In figure 1(B), the spectra of the implanted and thermally annealed samples are shown. All of the spectra

show broadened resonance lines centred at about -0.40 mm s^{-1} , with average widths of 0.55 mm s^{-1} . For the as-implanted samples, asymmetric broadening appeared suggesting the existence of another spectral component. This kind of broadening is more apparent for $x > 0.5$. The spectra could be fitted by assuming only two components. One is a quadrupole-split component with a distribution in the quadrupole-split (Q.S.) values, and the second is a broadened single line at -0.15 mm s^{-1} . The average I.S. (minus signs appear because of the source experiment), Q.S., and the standard deviation σ for the distribution of the quadrupole-split component, and the I.S. value for the single line, and the relative intensities are compiled in table 1. For the linewidth values of the quadrupole subspectra, 0.27 mm s^{-1} was found; for the single-line component, $0.42(1) \text{ mm s}^{-1}$ was found. After annealing the implanted samples at $800 \text{ }^\circ\text{C}$, the single-line component vanished in the spectra of the samples with $x = 0.48, 0.50$ and 0.52 . No other components could be resolved for the samples with the various concentrations.

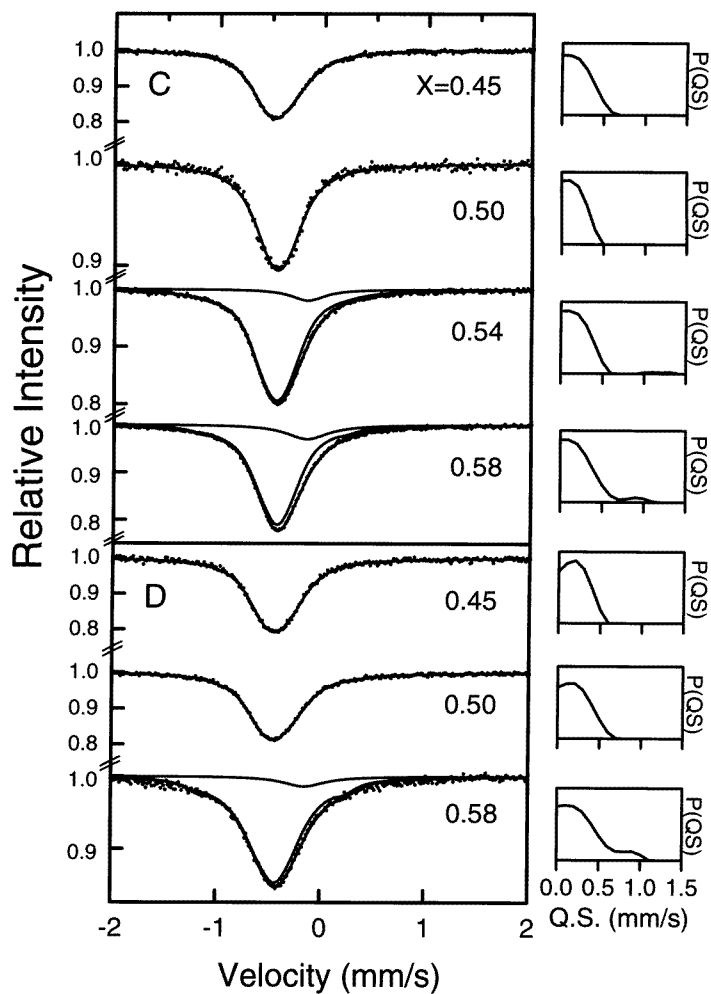


Figure 2. Mössbauer spectra of synthesized $\text{Co}_x\text{Ga}_{1-x}$ slowly cooled (C) and quenched (D) samples.

For comparison a detailed analysis was performed for the synthesized alloy samples in the broad concentration range of the B2 phase. The measured spectra for these samples are shown in figure 2.

The spectra are very similar to those of the implanted and annealed samples, indicating the complete recovery of the lattice after annealing. The spectra could be also fitted with a quadrupole-split component with a distribution, and a single line, but not with the predicted relative intensities, and I.S. and Q.S. values for 8Ga, 7Ga1Co, 6Ga2Co and 5Ga3Co nearest-neighbour configurations given in [7]. The parameter values obtained for the B2 alloys are compiled in table 1. Despite a number of new syntheses and treatments of the samples, we could not reproduce the spectrum of the sample with $x = 0.45$ given in [7] in which a component with I.S. = 0.23 mm s^{-1} and with the largest relative fraction appeared (the intensity at -0.23 mm s^{-1} was found to be too low). The position of the spectra of the samples in this concentration range measured by us excluded the existence of a component with a value of I.S. = 0.23 mm s^{-1} and with relative fraction above 50%. Therefore, the I.S. value of the iron with eight Ga neighbours is probably not -0.23 mm s^{-1} . We have measured the Mössbauer spectra of ^{57}Co in the CoGa_3 phase, where there are seven Ga atoms in the nearest coordination shell [10] of Co, and the values I.S. = $-0.32(1)$ and Q.S. = 0.13 mm s^{-1} were found. The single-line components appeared only for $x > 0.5$, as might be expected. The antistructure Co atoms carry local moments. A measurement made at 78 K on a sample with $x = 0.58$ resulted in a magnetic splitting with an 110 kOe internal-field value, in agreement with the result of Rao and Iyengar [11].

4. Discussion

At the present dose the implantation increased the Co concentrations in the implanted layer by an average of only 0.04 at.%. We attribute the high-intensity quadrupole-split doublet distribution to the ^{57}Co atoms in the Co sublattice. The $\langle\text{I.S.}\rangle$ value of this component is close to that expected for iron in the Ga nearest neighbourhood. I.S. = -0.37 mm s^{-1} was measured for ^{57}Co impurities in Ga metal [12]. The isomer shift systematics [13] shows -0.39 mm s^{-1} for iron in Ga. The $\langle\text{Q.S.}\rangle$ values are smaller than the Q.S. value (0.65 mm s^{-1}) [8] of the iron atom in the Ga sublattice having a vacancy in the nearest neighbourhood. The smaller Q.S. values indicate that the vacancies are in the Co sublattice in the second NN. Because of the low resolution and the correlation between the parameters, the contributions of the antistructure atoms and the vacancies to the lowering of the symmetry at the atomic sites cannot be separated. Only a small increase of the $\langle\text{Q.S.}\rangle$ and σ -values was observed for the quenched samples, indicating that the approximately 1.5 times higher vacancy concentration for the latter resulted in a relatively small effect on these parameters. Clustering of the vacancies might decrease their effect on the local distortion at the probe atoms. An indication on the clustering was observed in this alloy [14], where the relative fraction of the spectral component attributed to the iron–single-vacancy complex in the Ga lattice was about ten times less than can be expected on the basis of the vacancy concentration data [3, 5, 7]. Another explanation for the small quadrupole splitting with the distribution could be the presence of the lattice distortion around vacant Co sites perturbing the local symmetry to a greater or lesser extent (depending on the distance between the vacant and the probe atomic sites) in the Co sublattice. X-ray diffraction measurements on single crystals of CoGa alloys gave evidence of the distortion of the lattice [15]. Similar results, i.e. broadened absorption resonance lines with I.S. = 0.3 mm s^{-1} , were observed [8] for ^{57}Fe atoms in $\text{Ni}_x\text{Ga}_{1-x}$ alloys, where iron is located in the Ni sublattice. The widths of the spectra of our synthesized samples show concentration dependence. $\langle\text{Q.S.}\rangle$

and σ take their lowest values at $x = 0.50$, indicating that vacancies (predominantly for $x < 0.50$) and antistructure atoms (predominantly for $x > 0.50$) are responsible for the increase of these parameters. For quenched samples, larger $\langle Q.S. \rangle$ and σ -values were found because of the larger vacancy concentration and the higher degree of disorder. The $\langle I.S. \rangle$ values of the components did not change significantly with the concentration. The single-line component appeared only for $x > 0.50$, where antistructure Co atoms form in larger concentration. The spectra of the implanted samples are broader than the spectra of the synthesized samples; the broadening is larger for $x > 0.5$. The implantation increased the relative intensity of the broad single-line component. The broadening is probably caused by the effect of the increase of the number of the second-NN vacancies. We attribute the increase of the single-line component to the increase of the relative fraction of the Co atoms located in the Ga sublattice after implantation. After annealing the implanted samples, the single-line component appeared only at $x = 0.54$, indicating the reordering of the Co into the Co sublattice.

5. Conclusion

The implantation of ^{57}Co resulted in the broadening of the Mössbauer emission lines in $\text{Co}_x\text{Ga}_{1-x}$ alloys. This broadening can be attributed to the lowering of the local symmetry around ^{57}Co atoms by the creation of defects—vacancies—and the increase of the relative concentration of the antistructure Co atoms after implantation. The results of the new source experiments made on $\text{Co}_x\text{Ga}_{1-x}$ alloys are not in agreement with those published earlier by other authors and interpreted by using a lattice simulation model for the calculation of the fractional occurrence of the local atomic configuration around Co. The results showed for $x < 0.50$ weak concentration dependence of the hyperfine interaction parameters for the Co in the Co sublattice, indicating no significant changes in the nearest local structure around the Co atoms.

Acknowledgments

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