

## ELECTROSTATIC HYPERFINE INTERACTIONS IN $Y(Fe, Al)_2$

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Room temperature  $^{57}Fe$  Mössbauer and X-ray diffraction measurements are reported for  $Y(Fe_xAl_{1-x})_2$ ,  $0.1 \leq x \leq 0.9$ . For  $x \leq 0.65$  broadened and on the Al-rich side structured Bragg-peaks are observed. The asymmetry of the quadrupole split Mössbauer spectra depends on  $x$ . Whereas two different slopes are obtained for the concentration dependence of the mean quadrupole splitting on the Al- and the Fe-rich side, the isomer shift exhibits a smooth dependence on  $x$ , which can be correlated to the change in volume caused by the Al substitution.

The Laves phases  $Y(Fe_xAl_{1-x})_2$  crystallize in the cubic  $MgCu_2$  structure type except a small region around  $x = 0.55$  where the hexagonal  $MgZn_2$  structure type is stable. Whereas the mean effective moments per Fe atom are only mildly dependent on the Fe concentration, the mean spontaneous moments and the ordering temperatures decrease drastically with decreasing  $x$  on the Fe-rich side. For  $x \leq 0.78$  no long range magnetic order is observed. Short range order and freezing effects are detected for lower Fe contents at low temperatures pointing to mictomagnetism. The saturation moments for the calculated mean cluster exhibit a large difference on both sides of the hexagonal domain /1,2/.

In continuing these investigations a study of the electrostatic hyperfine interactions in connection with X-ray diffraction measurements were performed on the cubic samples at room temperature.

The series  $Y(Fe_xAl_{1-x})_2$ ,  $0.1 \leq x \leq 0.9$ , was prepared by high frequency melting in a water cooled copper boat using Ar as a protective atmosphere. Different amounts of Y excess were used to obtain single phased samples. The purity of the starting materials was 99.9, 99.99 and 99.999% for Y, Fe and Al, respectively. A standard Philips goniometer was used with a horizontal collimation of the primary beam of  $0.125^\circ$ . The Mössbauer measurements were performed with a constant acceleration type spectrometer. The source ( $^{57}CoPd$ ) was always kept at room temperature.

On the Fe-rich side, with the exception of  $x = 0.65$ , the line widths of the Bragg - peaks are approximately twice those measured for quartz which was mixed up with the powdered sample as a calibrating material. For  $x = 0.65$  an increase of roughly 30 % in line width was obtained and furthermore on the Al-rich side for all Fe containing samples the diffraction peaks were not only broadened but also structured. Since no additional lines could be detected, the existence of regular multilayers sequences, reported for Laves phases which ex-

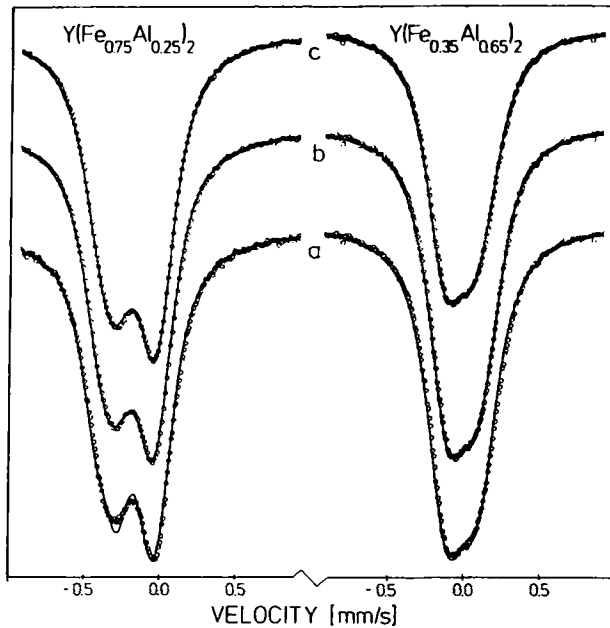


Fig.1. Room temperature  $^{57}\text{Fe}$  Mössbauer transmission spectra of typical  $\text{Y}(\text{Fe},\text{Al})_2$  samples. Full lines: spectra fitted by a superposition of two subspectra (a), a superposition of up to five subspectra with intensity ratios according to a binomial distribution taking into account nearest Fe neighbour environments (b) and a quadrupole distribution (c).

hibit a structural change from the cubic to the hexagonal structure type /3/ must be excluded. An analysis by taking into account a distortion of the  $\text{MgCu}_2$  structure type was not successful. Generally a distortion of approximately 1% was sufficient to obtain the observed line broadenings, however the resulting line intensities for the different diffraction peaks are in disagreement with the theoretically calculated ones for every selected type of distortion. From this the existence of regions with different Fe-concentrations may be a possible explanation. Since the lattice spacings increase linearly with decreasing  $x$  as an upper limit these differences can be estimated to 3 - 7%. These fluctuations of the Fe concentration are independent of both the conditions of the sample preparation and the excess of Y.

For  $0.85 \geq x \geq 0.10$  quadrupole split Mössbauer spectra were recorded at room temperature. The asymmetry of the shape of the spectra depends strongly on  $x$  ( Fig.1 ), pointing to an influence of the different environments of the Fe atoms not only on the hyperfine fields at low temperatures /2/ but also on the electrostatic interactions far above the temperature where the magnetic hyperfine splitting disappears ( $T_A$ ). Therefore three different methods were used to fit the spectra. As a first approximation they have been analyzed with a superposition of two subspectra. Because of the different values of the quadrupole splitting ( $Q$ ) and isomer shift ( $I_s$ ) observed at the Fe-rich and Al-rich side of the series the

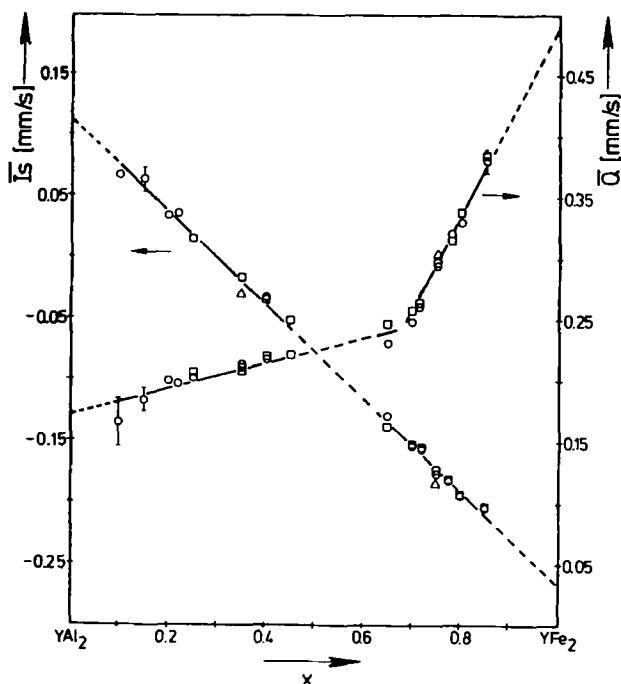


Fig.2. Concentration dependence of the mean quadrupole splitting  $\bar{Q}$  and the mean isomer shift  $\bar{I}s$  (relative to  $^{57}\text{CoPd}$ ) at room temperature (spectra fitted with two subspectra  $\circ$ , binomial distribution  $\square$ , quadrupole distribution  $\triangle$ ).

spectrum with the larger value of  $\bar{Q}$  was correlated with the lower value of  $\bar{I}s$ . The intensity ratio of the two subspectra varies continuously with  $x$ . However always some small deviations from the measured spectra remain (Fig.1). Therefore an analysis taking into account the different environments of nearest Fe neighbours by means of a binomial distribution was performed. The agreement of the fits is excellent (Fig.1). On the Fe-rich side the  $\bar{Q}$  values of the different environments decrease monotonically with decreasing  $x$  and can be correlated with  $\bar{I}s$  as in the former analysis. On the Al-rich side however no smooth behaviour could be obtained for  $\bar{Q}$  and no correlation with  $\bar{I}s$  which leads to a smooth concentration dependence was possible. Nevertheless the mean quadrupole splitting ( $\bar{Q}$ ) and the mean isomer shift ( $\bar{I}s$ ) are in good agreement with those of the first fitting procedure (Fig.2). These results strongly point to a quadrupole distribution which is also inferable from the  $\text{MgCu}_2$  structure, if the Al substitution and only nearest neighbour interactions are taken into account. For  $x = 0.75$  and  $x = 0.35$  a fit according to such a quadrupole distribution /4/ was performed. The allowed  $\bar{Q}$  values varied inbetween 0.00 (0.15) mm/s and 0.70 (0.40) mm/s on the Fe (Al) - rich side. In accordance with the calibration measurements the half width of the Lorentzian lines was allowed to vary between 0.22 and 0.26 mm/s. It was not possible to fit the spectra with only one value for  $\bar{I}s$ . Therefore as a first approximation a linear dependence of  $\bar{I}s$  on  $\bar{Q}$  according to  $\bar{I}s = A*(\bar{Q}-\bar{Q}_{\text{min}}) + B$  was used /4/ leading to a quadrupole distribution which depends strongly on these two parameters. The shape of the

resulting distribution, which is only meaningful if the mean square deviation was a minimum, is similar to a Gaussian one and about three times broader on the Fe-rich side than on the Al-rich. The  $\bar{Q}$  and  $\bar{I}_s$  values are in agreement with those of the other fitting models ( Fig.2 ).

On the Al-rich side the quadrupole distribution is small, the differences in the  $I_s$  values which result from the spread in the Fe concentration according to the X-ray investigations are also small compared with the line widths of the Mössbauer measurements. Therefore it is not possible to resolve the influence of the regions with the slight spread in Fe concentration in these measurements. Since it was not possible to separate the different hyperfine parameters for the different Fe environments only mean values were considered. On the Fe-rich side  $\bar{Q}$  decrease linearly with decreasing Fe content ( $\Delta\bar{Q}/\Delta x = 0.78$  mm/s ). Extrapolating to  $x = 1.0$  leads to  $\bar{Q} = 0.49$  mm/s in agreement with the value reported for paramagnetic  $YFe_2$  /5,6/ indicating that  $\bar{Q}$  is only slightly dependent on temperature. A nearly temperature independent quadrupole splitting was also observed for all  $x$  values for  $T_{A_2} < T < 300$  K. On the Al-rich side  $\bar{Q}$  is only mildly dependent on  $x$  ( $\Delta\bar{Q}/\Delta x = 0.11$  mm/s ). The intersection of the two linear regions ( Fig.2 ) is near  $x = 0.68$ . The large decrease of  $\bar{Q}$  appears in approximately the same concentration interval where the drastic changes of the magnetic properties were observed. The change in the slope of the concentration dependence of  $\bar{Q}$  seems therefore not to be caused by the appearance of the hexagonal structure type. The linear increase of the lattice parameter with decreasing  $x$  points to a concentration dependent volume available for the Fe atoms. A plot of the increase in  $I_s$  against the volume change, both taken relative to  $YFe_2$ , leads to a straight line indicating that a charge transfer from the substituted Al to the Fe atoms is of minor importance and that the increase in  $I_s$  with decreasing Fe content is mainly caused by the change in volume.

To sum up: A correlation between  $\bar{Q}$  and  $I_s$  was observed. Although two different slopes were obtained for the concentration dependence of  $\bar{Q}$  and on the Fe-rich side the width of the quadrupole distribution decreases drastically with decreasing  $x$ , the concentration dependence of  $I_s$  indicates that a charge transfer from Al to Fe is of minor importance.

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