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# MAGNETO-VOLUME EFFECTS OF $\gamma$-Fe PRECIPITATES IN Cu AND CuAl MATRICES

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We have determined the dependence of the magnetic transition temperature $T_N$ and of the magnetic hyperfine field $B_{hf}$ on particle volume and on matrix lattice parameter in coherent antiferromagnetic $\gamma$-Fe precipitates in $Cu_{100-x}Al_x$ matrices ($0 \leq x \leq 14$) by $^{57}$Fe Mössbauer spectroscopy and dc susceptibility measurements. The average particle diameter $d$ was determined precisely by transmission electron microscopy (TEM). The behavior of $T_N(d)$ and of $B_{hf}(d)$ at 4.2 K for $\gamma$-Fe in Cu is in agreement with a suggested structural phase transition at $T_N$ for $d \gg 20$ nm. Precipitates smaller than $d \sim 15$–20 nm show superparamagnetism. The saturation hyperfine-field (and consequently the atomic Fe moment) of $\gamma$-Fe was found to increase remarkably with increasing lattice expansion of the CuAl matrix.

Coherent fcc iron ($\gamma$-Fe) precipitates in Cu are antiferromagnetic at low temperature [1–4] with a low atomic moment (0.7 $\mu_B$) and a small magnetic hyperfine field $B_{hf} \sim 2$ T. The magnetism of $\gamma$-Fe is interesting under two aspects. First, the ground-state magnetic properties of fcc Fe depend strongly on atomic volume [5]. One can expect to increase the lattice parameter of coherent $\gamma$-Fe precipitates by adding Al to the Cu matrix, since the lattice constant of fcc $Cu_{100-x}Al_x$ alloys increases linearly with $x$ [6]. Second, the magnetic transition temperature $T_N$ of $\gamma$-Fe precipitates was found to depend strongly on particle size [4]. This effect has been ascribed to a structural phase transition [7, 8] at $T_N$ in coherent $\gamma$-Fe precipitates of 50–60 nm diameter. In order to study this size effect in more detail and to observe magneto-volume effects we have determined the dependence of $T_N$ and $B_{hf}$ on particle volume and on matrix lattice parameter in coherent $\gamma$-Fe precipitates in $Cu_{100-x}Al_x$ matrices ($0 \leq x \leq 14$) by $^{57}$Fe Mössbauer spectroscopy and dc susceptibility measurements. The average $\gamma$-Fe diameter $d$ was determined precisely by TEM [9, 10].

Our Mössbauer spectra of $\gamma$-Fe in pure Cu are similar to those reported earlier [2, 4]. In the magnetically ordered state the $\gamma$-Fe spectral component was least-squares fitted with a hyperfine-field-distribution $P(B_{hf})$. Details will be reported elsewhere [11]. An example for the temperature dependence of the average hyperfine field $\bar{B}_{hf}(T)$ obtained from $P(B_{hf})$ curves for larger (66 nm) and smaller (5.1 nm) $\gamma$-Fe precipitates in Cu is shown in fig. 1. $T_N$ was obtained from the intersection of two tangents on these curves. Obviously $T_N$ is lower for the smaller particles. The striking feature in our results for

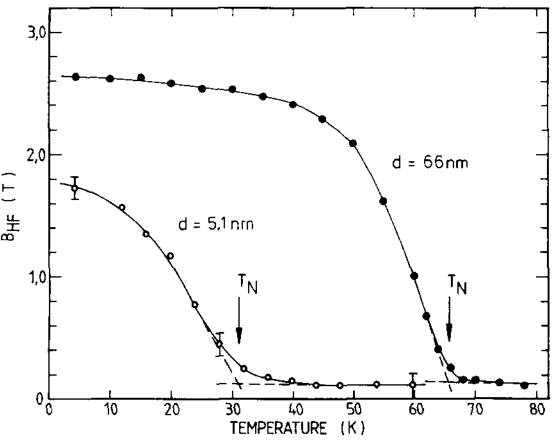

Fig. 1. Temperature dependence of average hyperfine field $\bar{B}_{hf}$ in $\gamma$-Fe precipitates. Upper curve: average diameter $d = 66$ nm, prepared from Cu–2.6 at%$^{57}$Fe alloy. Lower curve: $d = 5.1$ nm, prepared from Cu–0.43 at%$^{57}$Fe alloy.

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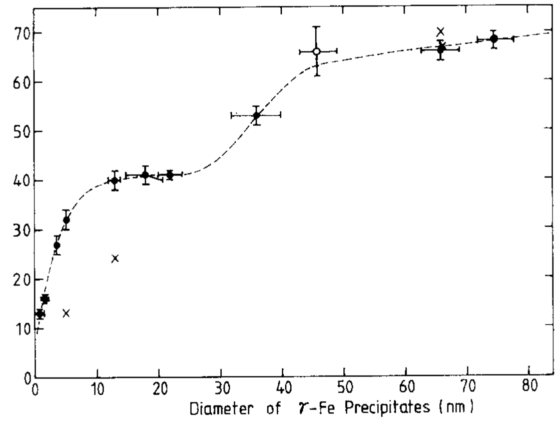

Fig. 2. Magnetic transition temperature $T_N$ versus average diameter $d$ of γ-Fe precipitates in Cu; circles: determined by Mössbauer effect; crosses: determined from dc susceptibility ($T_\chi$).

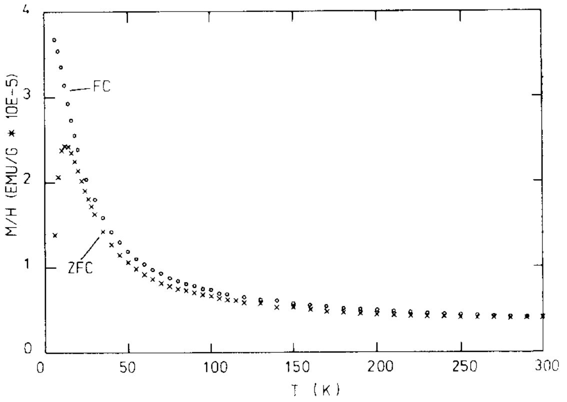

Fig. 3. Dc susceptibility versus temperature for 5.1 nm-diameter γ-Fe precipitates in Cu (same sample as in fig. 1). ZFC = zero-field cooled, FC = cooled in a field of 10 mT.

$T_N(d)$ is the stepwise increase of $T_N$ with rising particle diameter (fig. 2). We associate the steep increase of $T_N$ for $d \gtrsim 20$ nm with the reported structural phase transition [8] from fcc structure of small precipitates to a non-cubic distorted lattice structure with modulated antiferromagnetic spin structure in larger precipitates. The structural transition is revealed also in a stepwise increase of the most-probable field $B_{hf}^{peak}$ (4.2 K) from 1.6 T for $d \lesssim 20$ nm to 2.8 T for $d \gtrsim 20$ nm [11]. The sharp drop of $T_N$ below $d \sim 15$ nm (fig. 2) is caused by dynamic size effects, i.e., superparamagnetism of γ-Fe precipitates. This is shown by comparing $T_N$ values obtained by Mössbauer spectroscopy (fast time scale of ~ $10^{-7}$–$10^{-8}$ s) with transition temperatures, $T_\chi$, determined from dc susceptibility measurements by a SQUID (slow time of ~0.1 s) on the same samples. Figure 3 shows a representative susceptibility result. The peak in the zero-field-cooled (ZFC) susceptibility marks the "ordering temperature" (blocking temperature $T_\chi$) of γ-Fe in Cu with $d = 5.1$ nm. $T_\chi$ was found to be systematically lower than $T_N$ (fig. 2) for $d \lesssim 15$ nm (Cu matrix) and $d \lesssim 23$ nm (CuAl matrix).

Figure 4 shows representative Mössbauer spectra at 4.2 K of $Cu_{100-x}Al_x$–1.2 at% Fe alloys for various Al concentrations after precipitation-annealing at 460°C in $H_2$ gas for 4 h. Details of the sample preparation will be reported elsewhere [12]. As measured by TEM [10] this thermal treatment resulted in coherent γ-Fe precipitates with average diameters $d$ of 7–13 nm, depending on $x$ and the thermal history of the

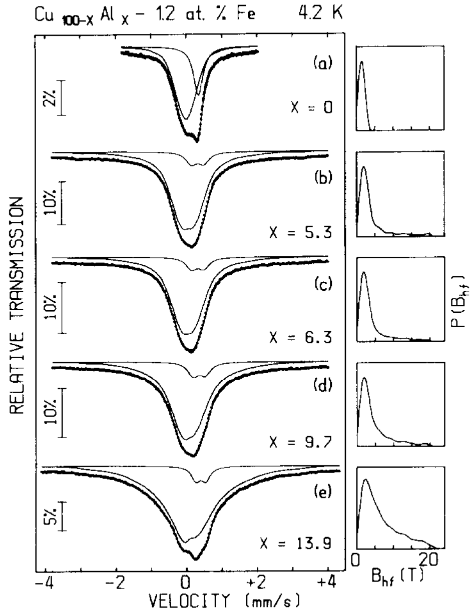

Fig. 4. Mössbauer spectra and corresponding hyperfine-field distributions $P(B_{hf})$ (right) of γ-Fe precipitates prepared from $(Cu_{100-x}Al_x)$–1.2 at% $^{57}$Fe alloy for different Al concentrations $x$.

sample. Unfortunately, $\gamma$-Fe precipitates in CuAl matrices have been found to contain dissolved Al atoms with a concentration $c$ which is about 3–5 at% less than the Al content $x$ of the matrix [12]. Therefore, the magnetic properties of these $\gamma$-Fe precipitates are influenced by a "chemical" effect due to dissolved Al impurity atoms in $\gamma$-Fe, superimposed to the magneto-volume effect caused by lattice expansion of the CuAl matrix. For $x = 13.9$ X-ray diffraction at 300 K yielded a lattice expansion of the $Cu_{86.1}Al_{13.9}$ matrix by 0.92% relative to pure Cu.

Two spectral components have been least-squares fitted to the spectra in fig. 4: a weak quadrupole-split line for Fe atoms dissolved in the CuAl matrix, and a strong broad component for $\gamma$-Fe precipitates fitted by a hyperfine-field distribution $P(B_{hf})$. The $P(B_{hf})$ curves show a low-field maximum at $B_{hf}^{peak}$ and a high-field tail, the latter becoming more pronounced with increasing $x$ (and increasing $c$), and depending only weakly on particle size [12]. We conclude, therefore, that the high-field tail is mostly due to a local "chemical" effect of Al impurities on neighboring Fe atoms in $\gamma$-Fe, and to a lesser extent to a magneto-volume effect. Mössbauer experiments in a strong, external field have shown that the high-field tail belongs to ferromagnetic Fe spins, while $B_{hf}^{peak}$ behaves as for rigid antiferromagnetic Fe moments [12]. The high-field tail leads to a strong increase of $\bar{B}_{hf}$ with $x$ (and apparently with matrix-lattice parameter, fig. 5). The value of $B_{hf}^{peak}$, however, was found to be independent of $c$ and of particle size [12]. $B_{hf}^{peak}$ increases with increasing $x$ and increasing lattice-parameter change (relative to pure Cu) with a slope $\sim +1.0\,T/(\%$ lattice-constant change) (fig. 5). The $B_{hf}^{peak}$-change is a real magneto-volume effect, being in agreement with high-pressure Mössbauer-effect results on our samples which yield a $\bar{B}_{hf}$-change of $\sim +1.2\,T/(\%$ lattice-constant change) at 4.2 K [13]. The increase in $B_{hf}^{peak}$ with rising lattice parameter (fig. 5) is an indirect and qualitative verification of the predicted atomic-moment increase with atomic volume in fcc Fe [5].

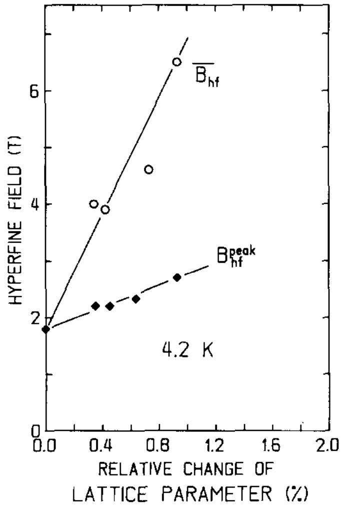

Fig. 5. Most-probable hyperfine field $B_{hf}^{peak}$ and average hyperfine field $\bar{B}_{hf}$ at 4.2 K of $\gamma$-Fe precipitates in $(Cu_{100-x}Al_x)$–1.2 at% $^{57}$Fe versus relative lattice-parameter change of the $Cu_{100-x}Al_x$ matrix.

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