MAGNETIC PROPERTIES OF THE SPINEL $ZnFe_2O_4$ IN CRYSTALLINE AND NANOSTRUCTURED MODIFICATIONS

RA-94-08, MÜNCHEN – JÜLICH – CANBERRA – JENA – LEIPZIG

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During the last four years we have investigated the magnetic properties of three differently prepared samples of the spinel $ZnFe_2O_4$ with μSR, neutron diffraction and Mössbauer effect measurements. In this contribution we provide a short summary of the results obtained.

The spinel structure is characterized by two different cation sites: the A sites are tetrahedrally and the B sites octahedrally coordinated by oxygens. The magnetic coupling between the Fe atoms by superexchange via oxygen atoms is weak within the A and the B sublattices whereas the A–B coupling is much stronger.

The first sample investigated had been *carefully annealed* during its preparation. Neutron diffraction measurements showed that in this sample the Fe ions only occupy the B sites in the spinel lattice (inversion $< 3\,\%$). As the B–B interaction is weak, the Néel temperature of this sample is low (T_N = 10.5 K). However, neutron diffraction and μSR experiments proved that already at much higher temperatures (~80 K) parts of the sample exhibit magnetic short range order. The correlation length of this short range order is only about 2.7 nm. The volume fraction of the short range ordered regions increases with decreasing temperature and reaches 75 % at T_N. At T_N the paramagnetic part of the sample orders antiferromagnetically. The volume fraction of the short range ordered part decreases rapidly below T_N. But even at the lowest measured temperature of 3 K about 20 % of the sample stays in a short range ordered state. The μSR experiments in longitudinally applied fields show that short range order and long range order are dynamic, producing field fluctuation rates at the muon site of at least 1.5 GHz.

The second sample was *rapidly quenched* during preparation. The inversion of this sample was determined to be 11 % by neutron diffraction. The neutron diffraction measurements show that the sample does *not* exhibit any magnetic long range order down to the lowest measured temperature of 2 K. Below ~25 K, however, one observes short range magnetic ordering of a part of the sample. This transition into a short range ordered state is also visible in μSR and Mössbauer effect data. The volume fraction of the short range ordered parts of the sample increases between 25 K and 10 K continuously with decreasing temperature. As the μSR data show, below 10 K the sample is magnetically short range ordered over its whole volume. With longitudinally applied fields part of the relaxation rate of the μSR signal could be decoupled at a temperature of 30 K. Therefore the fluctuation rate of the fields at the muon site must be much lower than in the annealed sample and can be estimated to be ~100 MHz.

Finally a *nanostructured* $ZnFe_2O_4$ sample was investigated. The average size of the particles in this sample is about 9 nm. The inversion was determined to be 44 %. At present two different explanations for the experimental observations are possible. In the neutron diffraction spectra an increase of intensity in some Bragg reflections is visible. This can be explained by ferromagnetic ordering of *part* of the sample, the Curie temperature being about 463 K. In the μSR spectra the ferromagnetic component is noticeable by a loss of initial asymmetry. Neutron diffraction and μSR data are fully consistent with an increase of the volume fraction of ferromagnetic ordered regions with decreasing temperature. This behaviour indicates a distribution of Curie temperatures in the sample caused by a broad distribution of particle sizes. The constant value of the initial asymmetry in the μSR spectra below 130 K can be explained by a critical particle size, below which magnetic ordering is not possible. The Mössbauer spectra show that the magnetic moments of the one–domain nanocrystals are not static but exhibits superparamagnetic fluctuations. The superparamagnetic fluctuations freeze out below 50 K. All observations can also be explained by the assumption that the missing magnetic moment in the neutron diffraction data at low temperatures is caused by the *special properties* of the nanostructured modification. In this case the reduced but constant signal in the μSR spectra at low temperatures has to be interpreted as 1/3 signal of the ferromagnetic phase extending over the *whole* sample. The spin–glas like behaviour below 50 K is also valid for this interpretation of the data.