H2. DIFFRACTION STUDIES OF MnO CONFINED IN NANOCHANNELS OF MESOPOROUS MATRICES.

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The properties of magnetics confined in nanometer scale cavities drastically differ from those in the bulk material. The investigation of model materials in the unusual conditions of a so-called “restricted geometry” is of fundamental interest since the confined geometry and the influence of the surface yield unusual properties.

During the past years, we carried out systematic studies of 3d-oxides in confinement, first in MnO confined in a vycor glass matrix with a random network of pores [1] then in MnO confined in MCM-41 or SBA matrix with a regular system of nanochannels [2,3,4] and MnO confined in MCM-48 matrix with a gyroidal channel system [5]. These amorphous silica matrices known as molecular sieves were discovered in 1992 and attracted much attention. They do not produce Bragg reflections and are very suitable to diffraction studies. Oxides within the matrix cavities were synthesized from solutions by the "bath deposition method". The high specific surface of the matrices and the good wetting of the channel walls by the liquid solution ensure that MnO predominantly occupies the channel voids.

Since the discovery of antiferromagnet order in MnO in 1949, this oxide has been the subject of intense experimental and theoretical interest. In MnO the antiferromagnetic order, which appears at 117 K by a first order phase transition, is accompanied by a rhombohedral contraction of the cubic lattice. In the magnetic structure, which consists of ferromagnetic sheets stacked antiferromagnetically along the (111) axis, the moments in the first coordination sphere are frustrated. Greenwald and Smart in the early 50's suggested that the distortion removes the frustration. So the structural distortion and the magnetic ordering in MnO are mutually dependent.

Shape of the nanoparticles.

Neutron diffraction and x-ray synchrotron experiments showed that, in contrast within the porous glass where MnO forms isotropic aggregates, inside the channel type matrices MnO forms nanowires or nanoribbons. In the latter, the two-dimensional character of the diffracting objects leads to a specific lineshape known as a "saw-tooth" profile and to a specific shift from the Bragg position towards larger diffraction angles. This yields an “effective” lattice parameter which is systematically lower than the corresponding lattice parameter of the three-dimensional lattice.

The profiles measured at the synchrotron source LURE were compared with those calculated numerically for objects of different dimensions using the Debye formula (Figure 1,2). This analysis allowed us to estimate the dimensions of the nanoparticles, which appear to be thin (~10 Å) ribbon or wire-like structures. In all cases, the nanoparticle lengths are in the interval of 180–260 Å, increasing with the channel diameter [2].

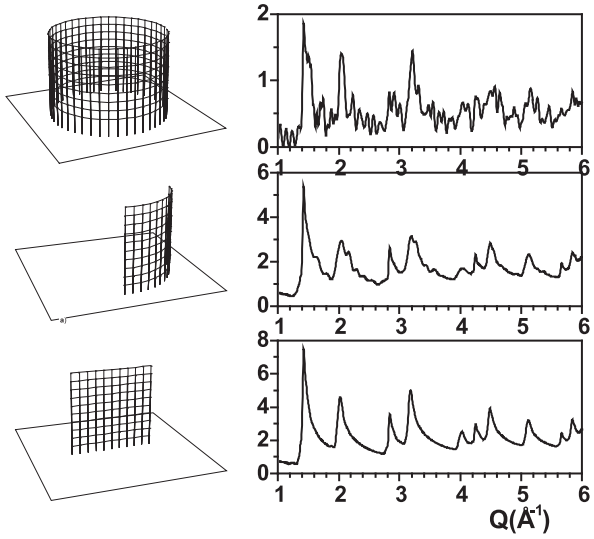

Figure 1. Numerical simulation of diffraction patterns from diffracting objects of different shapes.

Magnetic order and phase transition.

Neutron diffraction studies of confined MnO, performed at the diffractometer G6-1 showed that the magnetic structure is similar to the structure in the bulk.

However, the volume-averaged magnetic moment of confined MnO appears to be noticeably smaller than the moment in the bulk. This is a well known phenomenon in confined magnets, which is explained by the disorder of the magnetic moments at the surface.

In all type of matrices, the magnetic transition in confined MnO becomes continuous with a Néel temperature T_N enhanced with respect to the bulk [1,3]. Such behavior is well known as a finite-size "rounding" of the phase transition and results from the limitation of the correlation length by the nanoparticle size.

The observation of an enhanced Néel temperature is surprising, since a common effect expected in all nanostructured material is the decrease of T_N when the correlation length becomes limited by the nanoparticle size. In the present case, the magnetic disorder and the violation of the translation symmetry at the nanoparticle surface result in a small surface ferromagnetic moment whereas the core remains antiferromagnetically ordered. Taking into account the

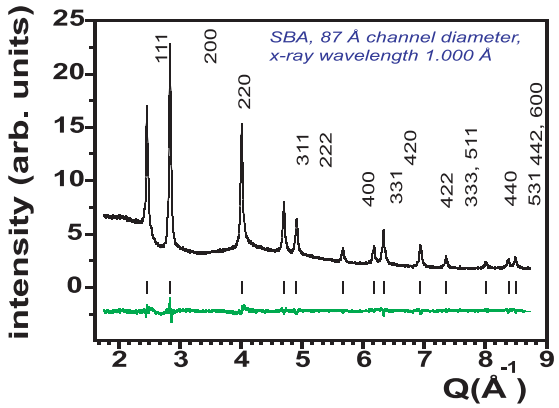

Figure 2. Observed x-ray diffraction pattern of MnO confined in SBA matrix with 87 _ channel diameter; in green, the difference pattern

ternary interaction of the non-critical ferromagnet, a critical antiferromagnetic behavior and the associated structural order parameters, the enhanced T_N can be explained within the framework of the Landau theory [3].

In MnO within channels of MCM-41 matrices, the critical exponent in the temperature dependence of the magnetic moment decreases with decreasing the channel diameter. We attribute the observed change of the magnetic transition to the increasing anisotropy and the change in the dimensionality of the magnetic system to a quasi-one-dimensional case (Figure 3).

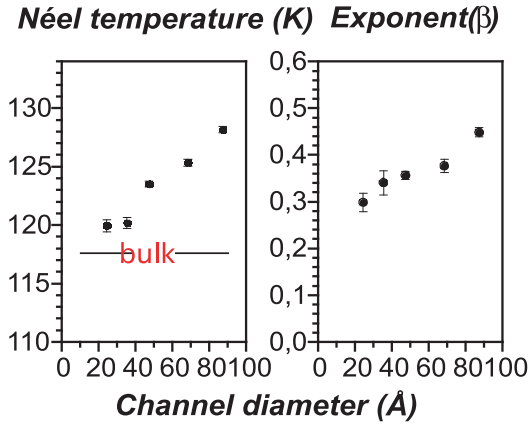

Figure 3. Dependences of the Néel temperature and critical exponent b with the channel diameter, as calculated by fitting the data with a power law.

Structural distortion and magnetic order.

According to conventional theory, antiferromagnetism in MnO is stabilized by the structural distortion. However, in the case of nanoparticles, the high anisotropy and the inner stresses add new terms to the free energy, which could drastically change the energy balance.

Interestingly, low temperature high-resolution x-ray diffraction experiments, performed in ESRF on nanoparticles of MnO confined in MCM-41 matrix with 35 Å channel diameter, showed a new structural transition at about 60 K, well below the Néel transition which occurs at about 120 K. At this second transition, the structural distortions which appeared below T_N suddenly disappear and the structure becomes cubic as in the paramagnetic region. This "reentrant" transition is accompanied by an increase of the lattice parameter, of the amplitude of atomic motion and the appearance of inner stresses (Figure 4). Surprisingly, there is no change in the temperature dependence of the magnetic moment associated with the low temperature transition. Such behavior drastically differs from the behavior known for the bulk.

Loss of long-range atomic order in MnO confined in MCM-48 matrix with a gyroidal system of channels.

The matrix MCM-48 is marvelous because the channels piercing in its amorphous silica body comply with the symmetry of the cubic space groups. The channel wall surface exactly follows the so-called "periodic minimal surface", forming a gyroidal structure with a three-dimensional network of channels.

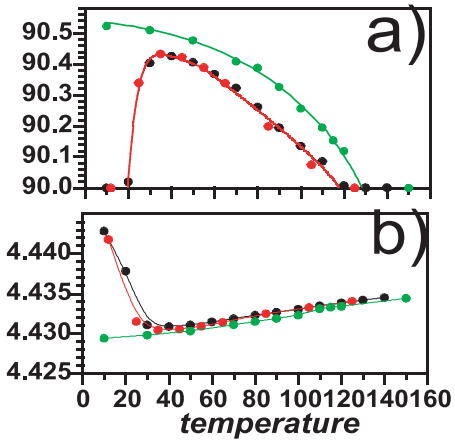

Figure 4. Temperature dependences of the angle of rhombohedral distortion (alpha) and the unit cell parameter.

Synchrotron X-ray experiments preformed at ESRF showed that the nanoparticles of MnO have a ribbon-like shape with a length of about 50 Å and do not show long-range atomic ordering. In spite of the disordered atomic structure, a phase transition from the cubic structure accompanied with a rhombohedral distortion was observed, like in the bulk material. The parameters of the phase transition appear to be similar to the parameters of the transition observed in MnO within the MCM-41 matrix, where atomic ordering extends over much longer length scales [5].

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