Magnetic phase transition in CoO confined to a vycor type porous glass. Neutron diffraction study.

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Neutron diffraction studies of antiferromagnetic CoO confined to a vycor type porous glass demonstrate a continuous magnetic phase transition with a decreased Néel temperature and reduced magnetic moment as compared with the bulk.

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I. INTRODUCTION

The behavior of the nanostructured substances in the conditions of so-called "restricted" or "confined" geometry has attracted great fundamental and practical interest because of their potential use for technological application. One of the most interesting problems is magnetism in confinement.

Oxides of the transition 3d-metals as MnO and CoO are especially interesting for such investigations. They have a similar antiferromagnetic structure. In MnO the magnetic moments lay within the (111) plane, while in CoO they tilted out from this plane\(^1\). This leads to different magnetic symmetry that results in different magnetic behavior: in MnO the magnetic order appears by a first order transition while in CoO it does by a second order transition\(^4\). The magnetic transition in MnO is accompanied by a rhombohedral crystal distortion which stabilizes an antiferromagnetic structure. In CoO one observes a strong tetragonal distortion accompanied by a small trigonal distortion\(^6\). At last in MnO the orbital magnetic moment is practically "frozen", while in CoO the large orbital contribution is observed\(^7,8\).

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After the neutron diffraction experiments with antiferromagnet MnO embedded in a porous glass\(^9\) we performed the experiments with CoO synthesized within the similar porous matrix. Our objective was to compare the behavior of these oxides in the conditions of "restricted" geometry.

II. EXPERIMENT

As well as in the case of MnO the host porous matrix was made from a sodium borosilicate glass\(^10\). The matrix has a random interconnected network of elongated pores\(^11\) with a narrow distribution of pore diameters of 70(3) Å. CoO was synthesized from a cobalt nitrate solution by a chemical, "bath deposition" method.

The chemical instability of CoO in the conditions of high dispersed nanoparticles with large ratio surface/volume strongly increases. Therefore without special precautions CoO oxidizes after about a year in practically stoichiometric Co$_3$O$_4$.

Because of small quantity of CoO embedded within nanopores the signal is weak. Therefore for measurement of magnetic reflections at low angles of diffraction we used the high luminosity diffractometer G6-1 of the Laboratoire Léon Brillouin with a large neutron wavelength of 4.73 Å. For measurements of nuclear reflections we used diffractometers with better resolution and smaller neutron wavelength G4-1 of the Laboratoire Léon Brillouin and E9 of the Hahn-Meitner-Institut with neutron wavelengths 2.43 Å and 1.80 Å, respectively.

III. RESULTS AND DISCUSSION

Neutron diffraction patterns (figure\(^1\)) show the crystallizing of the CoO within nanopores. The amount of the impurity phase Co$_3$O$_4$ (its reflection is shown by an arrow in figure\(^1\)) does not exceed some percents.

From the peak broadening the volume-averaged diameter of the embedded nanoparticles was estimated as 100(5) Å. This value is larger than the mean pore diameter 70 Å, showing that the confined oxide CoO, similar MnO, forms interconnected aggregates rather than isolated nanoparticles. It demonstrates that the crystallization spreads over at least several adjacent pores. The measured averaged diameter turns out to be smaller than the nanoparticle diameter of 140 Å found in the embedded MnO, that is connected with different wetting ability of two oxides.
1.0 1.5 2.0 2.5 3.0 3.5 4.0
12
14
16
Q (Å)\(^{-1}\)

FIG. 1: Neutron diffraction patterns from CoO confined within a porous glass, observed (closed circles) and calculated (solid line). Diffractometer G4-1, temperature 10 K.

The indexing of the observed magnetic reflections below 280 K corresponds to antiferromagnetic ordering of type-II in the fcc lattice similar to the bulk CoO\(^1,2\). The collinear magnetic moments were found tipped out of the (111) plane 9(3)° that is consistent with the reported value for the bulk \(^3\).

From the magnetic Bragg reflections, the ordered magnetic moment at 10 K was found to be 2.92(2) \(\mu_B/\text{ion}\). This volume-averaged value is smaller than the value of 3.80 (1) \(\mu_B/\text{ion}\) measured for the bulk CoO\(^3\). The similar phenomenon was observed for MnO embedded within different porous media and was attributed to the disordering of moments at the surface of nanoparticle\(^9,12\).

The observed structure distortions was found to be the same as in the bulk, namely, at the lowest temperature the tetragonal distortion (a-c)/c, (here a and c are lattice parameters) in confined CoO is 0.0114(7) that well coincides with that measured for the bulk\(^7\). Small trigonal distortion observed in the synchrotron radiation experiments is 100 times weaker than tetragonal distortion and is beyond of the accuracy of our experiment\(^6\).

In spite of rich history of experimental and theoretical studies of the bulk CoO the data about its critical behavior are controversial. This oxide is traditionally considered as a classic example of compound with a large unquenched orbital moment. Therefore its magnetic behavior should follow to the prediction of the 3D-Ising model with critical exponent \(\beta = 0.312\) (or 5/16), that was shown experimentally in the specific heat measurements\(^13\).

The birefringence measurements of\(^14\) showed the close value of \(\beta = 0.29(2)\). However, the neutron diffraction with a single crystal displayed \(\beta = 0.25(2)\) only\(^4\). To explain this disagreement the phenomenological correction for the tetragonal lattice contraction below \(T_N\) was proposed, which raises \(\beta\) to values of 0.29(2)\(^4\).

Moreover, in ref\(^6\) the authors found upon the symmetry breaking from cubic to monoclinic symmetry in the bulk CoO concluded that the magnetic transition is discontinuous but with very small first order jump.

In figure 2 the temperature dependence of the magnetic moment for confined CoO is shown. Fitting the observed dependence with a power law

\[
m(T) = m_0(1 - T/T_N)^\beta
\]

yield the value \(\beta = 0.31(2)\). This value of \(\beta\) should be compared with the uncorrected for contraction value of 0.25(2) measured for the bulk\(^4\). The increasing of the critical exponent in confinement one can explain by the well known effect of the finite-size rounding of the phase transition\(^15\), which leads to a smearing up the transition that, in turn, goes to increasing of the critical exponent.

Surprisingly, the measured value of \(\beta\) in confinement appears to be close to the expected value for the bulk 3D-Ising model, however it is smaller than the critical exponent of 0.362(4) calculated by a computer simulation of the finite-size scaling for 3D-Ising model\(^16\).

Néel temperature \(T_N = 278(0.5)\) K turns out to be decreased as compared with the bulk value of 289.0(1) K\(^4\). It is a common effect expected for nanostructured magnets\(^17,18\), resulted from the limiting of the correlation length by the nanoparticle size. However in MnO confined in the same porous media \(T_N\) was found enhanced with respect to the bulk\(^9,12\). 

FIG. 2: Temperature dependence of the magnetic moment and its fitting with a power law. In the inset the log-log graph is shown. It is seen that two points nearest to \(T_N\) have a large contribution from quasi-elastic scattering.
There are some competitive factors which influence the transition temperature. The decreasing the correlation length in nanostructured objects leads to a decrease of $T_N$. However there is another mechanism of the ternary interactions of the structural and magnetic order parameters which can lead to an increase of $T_N^{12}$. Apparently the relative role of these two factors is different for two oxides CoO and MnO.

In conclusion, by using neutron diffraction the magnetic order was observed for antiferromagnet CoO embedded in a porous glass. The type of magnetic order and structural distortion in nanostructured CoO was found to be the same as in the bulk. The ordered magnetic moment is noticeably smaller than in the bulk. The magnetic phase transition was found to be continuous as in the bulk, however with decreased $T_N$ and slightly increased critical exponent that attributed to size-effect rounding of a phase transition in confinement.

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