Stabilization of Transition Metal Chromite Nanoparticles in Silica Matrix

Jiri Plöcek, Petr Holec, Simona Kubickova, Barbara Pacakova, Irena Matulkova, Alice Mantlikova, Ivan Nemec, Daniel Niznansky, Jana Vejpravova

Abstract—This article presents summary on preparation and characterization of zinc, copper, cadmium and cobalt chromite nanoparticles, embedded in an amorphous silica matrix. The ZnCr$_2$O$_4$/SiO$_2$, CuCr$_2$O$_4$/SiO$_2$, CdCr$_2$O$_4$/SiO$_2$ and CoCr$_2$O$_4$/SiO$_2$ nanocomposites were prepared by a conventional sol-gel method under acid catalysis. Final heat treatment of the samples was carried out at temperatures in the range of 900–1200 °C to adjust the phase composition and the crystallite size, respectively. The resulting samples were characterized by Powder X-ray diffraction (PXRD), High Resolution Transmission Electron Microscopy (HRTEM), Raman/FTIR spectroscopy and magnetic measurements. Formation of the spinel phase was confirmed in all samples. The average size of the nanocrystals was determined from the PXRD data and by direct particle size observation on HRTEM; both results were correlated. The mean particle size (reviewed by HRTEM) was in the range from ~4 to 46 nm. The results showed that the sol-gel method can be effectively used for preparation of the spinel chromite nanoparticles embedded in the silica matrix and the particle size is driven by the type of the cation A$^{2+}$ in the spinel structure and the temperature of the final heat treatment. Magnetic properties of the nanocrystals were found to be just moderately modified in comparison to the bulk phases.

Keywords—Chromite, Fourier transform infrared spectroscopy, magnetic properties, nanocomposites, Raman spectroscopy, Rietveld refinement, sol-gel method, spinel.

I. INTRODUCTION

CHROMITES with A$^{2+}$Cr$_3$O$_4$ formula are binary oxides, where A$^{2+}$ and Cr$^{3+}$ are cations occupying tetrahedral (A) and octahedral (B) sites, respectively. The chromites are considered as materials with variety of potential applications ranging from high-temperature ceramics [1], catalysis [2], semiconductors [3]–[6] to electrochemical sensors [7]. At high-enough temperatures, the chromites crystallize in a cubic structure (space group Fd-3m), with 56 atoms per unit cell (Z = 8). The 3d$^3$ electron configuration of Cr$^{3+}$ is very stable because each of the t$_2g$ energy level is singly occupied, so there is no tendency of site mixing or lattice distortion at the transition temperature. The magnetic ordering is therefore characteristic by a considerable spin frustration and strongly depend on the chemical order (the spinel inversion, oxygen deficit etc.) and on the cation site occupancy in the spinel structure [8] (diamagnetic, paramagnetic or JT active), respectively.

The zinc chromite is known as a frustrated antiferromagnet with a complex coplanar spin structure below the Neél temperature, $T_N = 12$ K [9] and it is arguably the most magnetically-frustrated system known so far. At room temperature, it has a cubic crystal structure where Cr$^{3+}$ ions form a network of pyrochlore-like lattice [10]. The Curie-Weiss temperature is about 390 K, indicating strong antiferromagnetic frustration, yet chromium spins remain in a cooperative paramagnetic phase down to the $T_N$. There, a first-order phase transition from a cubic paramagnet to a tetragonal antiferromagnet signals the end of distinct spin and lattice degrees of freedom. It is a unique example of the so-called spin Jahn-Teller system [11].

The other example with a diamagnetic cation, the cadmium chromite exhibits an elliptical spiral magnetic structure below the $T_N = 7.8$ K and simultaneously reveals a dielectric anomaly at the $T_N$ [12]. The CdCr$_2$O$_4$ also undergoes a spin-Peierls-like lattice distortion at the $T_N$ [13], [14]. The lattice symmetry is lowered from cubic to tetragonal; the lattice is elongated along the c-axis, while it shrinks in the same direction in the ZnCr$_2$O$_4$. It is also surprising that the magnitude of the distortion is larger in the Zn compound with weaker magnetic interactions.

While less common, tetrahedral Cu$^{2+}$ on the A site of the spinel network also displays JT activity, with the relatively high JT temperature, $T_{JT} = 830$ K, resulting in the tetragonal structure (space group I4$_1$/amd). This distortion lowers symmetry by compressing the tetrahedron and thereby breaking the degeneracy of the partially-occupied t$_2$ energy levels [15]. Magnetic properties of the copper chromite have been rarely investigated, it is reported as a hard ferromagnet with the Curie temperature, $T_C = 135$ K.

Cobalt chromite samples with magnetic Co$^{2+}$ (d$^7$) cations develop below $T_C = 94$ K long-range ferrimagnetic order, and moreover exhibits a sharp phase transition at $T_S = 27$ K to the onset of long-range spiral magnetic order [16], [17]. Magneto-capacitive measurements show that the dielectric constant of CoCr$_2$O$_4$ couples to the spiral magnetic order parameter, but is insensitive to the ferrimagnetic spin component [18].
As is known, the magnetic properties such as saturation magnetization, remanent magnetization and coercivity, respectively, depend strongly on the particles size and microstructure of the materials. In case of the spinel chromites, significant change of magnetic order and hence dielectric response is expected upon reduction of the particle size below a coherence length of the spiral component of the magnetic structure [17], [19]. Therefore it is important to use a proper technique by which both the size and the shape of particles can be well controlled. One of the ways to prepare the nanocrystals with the required properties represents the sol-gel method [20], [21]. The advantages of this method are namely a good homogeneity of the final materials, low temperatures of the treatment, and control of the particle size by final heat treatment. On the other hand, to stabilize a ternary spinel phase in silica matrix, which has an acidic nature, is a challenging task.

In this work we focused on optimization of the fabrication procedure in order to obtain single phase transition metal chromite nanoparticles, embedded in the silica matrix. The optimized samples were investigated by varied of experimental techniques and results of structure characterization and magnetic properties are presented. Moreover, the impact of the size reduction on magnetic order in selected ACr2O4 is also discussed.

II. EXPERIMENTAL

A. Materials Preparation

The conventional sol-gel method using TEOS, HNO3 as an acid catalyst, formamide as a modifier, and methanol as a solvent, was used for preparation of the nanocomposites. The sol was prepared by dissolving of the corresponding amount of the Cr(NO3)3·9H2O and the Zn(NO3)2·3H2O, Cd(NO3)2·2H2O, or Co(NO3)2·6H2O, respectively, in methanol. The Si/ Cr molar ratio was 5/1, which corresponds to the SiO2/ACr2O4 (where A = Zn, Cu, Cd, and Co) molar ratio of 10/1. The gelation time was approximately 24 h at 40°C. The samples were left at 48 h for ageing. Then they were progressively dried at 40°C for 2 days in flowing N2-atmosphere. After drying, they were preheated first at 300°C in a vacuum for 2 h and then at various temperatures (900, 1000, 1100, 1200°C) under normal atmosphere. The samples were heated for two hours at the above-mentioned heating temperatures.

B. Materials Characterization

The final products were characterized at room temperature using the Bragg- Brentano geometry on a Philips X’pert PRO MPD X-ray diffraction system equipped with a ultra fast X’Celerator detector using Cu-anode (Cu Kα, λ = 1.5418 Å). The particle diameters (mean size of the coherently diffracting domain) and lattice parameters were obtained using the Rietveld refinement within the program FullProf software [22] where the instrumental broadening was eliminated by measuring the calibration standard (in our case, the LaB6 was used).

The size and shape of prepared nanocomposites were analyzed on a HRTEM JEOL JEM 3010 (High-Resolution Transmission Electron Microscope). Particle size distribution was obtained by manual measurement and statistical evaluation of large-scale projected images. Elemental composition of nanoparticles was verified by EDS (Energy-dispersive X-ray spectroscopy) analysis.

The infrared spectra were recorded on a Thermo Scientific Nicolet 6700 FTIR spectrometer (2 cm⁻¹ resolution, KBr beamsplitter, DTGS detector, Happ-Genzel apodization) in the 400 - 4000 cm⁻¹ region using nujol mull (KBr windows) technique. The FAR IR spectra were recorded down to 50 cm⁻¹ (4 cm⁻¹ resolution, Solid SubstrateTM beamsplitter, DTGS detector, Happ-Genzel apodization) in PE pellets.

The Raman spectra were recorded on a Thermo Scientific DXR Raman Microscope interfaced to an Olympus microscope (objective 50x) in the 50-1900 cm⁻¹ spectral region with ~3 cm⁻¹ resolution. The power of frequency-stabilized single mode diode laser (780 nm) impinging on the sample was ranging from 1 to 4 mW. The spectrometer was calibrated by software-controlled calibration procedure using multiple neon emission lines (wavelength calibration), multiple polystyrene Raman bands (laser frequency calibration) and standardized white light sources (intensity calibration).

Magnetic properties were measured using a commercial 7 T - SQUID magnetometer (MPMS by Quantum Design) in the temperature range 2 - 350 K.

III. RESULTS AND DISCUSSION

A. Powder X-ray Diffraction Measurement

The PXRD measurements were carried out on all samples and are shown in Fig. 1. Phase compositions (of selected samples) are summarized in the Table I. All samples contained spinel phase, together with the other impurity phases in some cases, as will be discussed further. In some samples, the shape of the spinel phase diffraction peaks with the steep Lorentzian like and the broad Gaussian- like components was detected, suggesting that the diffraction pattern is the superposition of two patterns representing two different size fractions of particles within the spinel phase. In case of unimodal particle size distribution, the crystallite size could be determined by analysis of the broadening of diffraction peaks using the well-known Scherrer equation [23] in the simplest approximation. Because of the complexity of the diffraction patterns, this approach would be absolutely inappropriate and would give average weighted diameter of both phases of different particle size. Therefore, the Rietveld refinement has been used for the calculations of the proper crystallite size. The results were in accordance with results obtained from direct particles observation by HRTEM. An overview of the chromite particle size, the phase composition of the samples and the determined lattice parameters is written in the Table I. The lattice parameters, a are in good agreement with those observed by other authors [24], [25].
The analysis of the data demonstrated that the samples that contain spinel as the single phase were the ZnCr$_2$O$_4$/SiO$_2$-1100 °C, CoCr$_2$O$_4$/SiO$_2$-1000 °C and the CoCr$_2$O$_4$/SiO$_2$-1100 °C samples. In the other samples, even with the spinel as the major phase, the presence of other metal oxides and/or the crystalline SiO$_2$ was detected. The content of the spinel phase increases with increasing annealing temperature up to 1100 °C, and further decomposition for the sample annealed at higher temperature (the CdCr$_2$O$_4$/SiO$_2$-1200 °C sample) was observed. The SiO$_2$ remained amorphous for all Zn, Co and Cu samples except the CuCr$_2$O$_4$/SiO$_2$-1100 °C. In case of the Cd samples, the SiO$_2$ was crystalline, with evident transformation from the α-quartz phase to the α-cristobalite at 1100 °C. The 1100 °C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase Comp.a</th>
<th>$d_{HRTEM}^b$ (nm)</th>
<th>$d_{PXRD}^c$ (nm)</th>
<th>Space Group</th>
<th>$a^d$ (Å)</th>
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<td>-</td>
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<tr>
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<td>(ZnO)</td>
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<td>ZnCr$_2$O$_4$</td>
<td>9; (11.2)</td>
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<td>8.3263</td>
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<tr>
<td></td>
<td>Cr$_2$O$_3$</td>
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<td>-</td>
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<td>11, 21; (15.0)</td>
<td>10.2; 20.1</td>
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</tr>
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<td>5.1; 25.2</td>
<td>Fd-3m</td>
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</tr>
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<td>7; (6.9)</td>
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<td>-</td>
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<td>-</td>
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<td>CuCr$_2$O$_4$</td>
<td>9, 21; (9.3)</td>
<td>28</td>
<td>I 4$_1$/amd</td>
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<tr>
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<td>Cr$_2$O$_3$</td>
<td>-</td>
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</tr>
<tr>
<td>CuCr$_2$O$_4$/SiO$_2$-1100 °C</td>
<td>CuCr$_2$O$_4$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

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*a* Phase composition of prepared samples ordered with decreasing content; in parenthesis phases with trace amount are mentioned.

$^b$ $d_{HRTEM}$ are maxima (modes) of particle size distributions determined by HRTEM; in parenthesis the mean chromite particle size is shown.

$^c$ $d_{PXRD}$ are chromite particle sizes determined from PXRD using the Rietveld refinement.

$^d$ $a$ denotes lattice parameters of chromite nanocrystals.

$^e$ $a$ denotes two different a-parameters which are corresponding to two different particles with different particle sizes.

Note: The sign ‘-’ means that the value was not measured or calculated.
The results of the PXRD analysis suggest, that the spinel chromites are formed as a kinetically preferred form in our systems. Silicates were observed as a minority phase only in samples with cadmium (the most basic), and their amount varied depending on the heat treatment, with the preferential abundance at low temperature.

B. HRTEM observation

In order to give the complete information about the crystallite size and morphology, the detailed HRTEM investigation of selected nanocomposite samples was performed. The mean particle size in each sample was evaluated from several different images by statistical analysis of diameter of about 100-300 nanoparticles. For all HRTEM images, the dark parts represent the chromite nanocrystals (or crystalline oxide phases) and bright parts correspond to the amorphous silica matrix. In Fig. 2, the HRTEM images of the ZnCr$_2$O$_4$/SiO$_2$ samples annealed at 1000 and 1100 °C, CdCr$_2$O$_4$/SiO$_2$ annealed at 1100 °C, CoCr$_2$O$_4$/SiO$_2$ annealed at 1000 and 1100 °C and CuCr$_2$O$_4$/SiO$_2$ annealed at 1000 °C are depicted. Generally, the chromite particles are in all the samples more or less of spherical shape, as has been also suggested by PXRD measurements, where no shape anisotropy has been observed. The histograms with depicted particle size distributions are placed below the HRTEM images. There is an apparent wide and unsymmetrical particle size distribution, hence the maximum at particle size distribution curve (statistical mode) is more significant than usually used mean of the particle size value. There are also observable two maxima in some cases distribution is bimodal. Both type of the particle diameters, mode and mean, are depicted in the Table I.

As can be seen from the distribution of the particle size depicted in Fig. 2, the zinc nanocomposites heated at 1000 °C show a mode of particle size of 9 nm, whereas the zinc nanocomposites heated at 1100 °C show bimodal distribution with maxima at 11 and 21 nm, respectively. Particle size distribution of cadmium nanocomposite heated at 1100 °C is trimodal with observed maxima around 7.5, 32.5, and 87.5 nm, but the maximum at 32.5 nm is not so clear due to relatively small statistical ensemble. The particles of the cobalt chromite are very well defined and they did not exhibit a diffused appearance suggesting insufficient crystallinity. The modes of particle sizes of the CoCr$_2$O$_4$ nanocrystals treated at 1000 °C were found to be 5 and 25 nm. The particle size of the sample heated at 1100 °C moderately increased with increasing temperature as expected, and was determined as 7 nm. The HRTEM result for the CuCr$_2$O$_4$/SiO$_2$ sample annealed at 1000 °C is shown in Fig. 2. The maxima at particle size distribution of this spinel phase treated at 1000 °C were observed at 9 and 21 nm. The results of the observation particle size distributions are placed below the HRTEM images. There is an apparent wide and unsymmetrical particle size distribution, hence the maximum at particle size distribution curve (statistical mode) is more significant than usually used mean of the particle size value. There are also observable two maxima in some cases distribution is bimodal. Both type of the particle diameters, mode and mean, are depicted in the Table I.
Fig. 2. The HRTEM images and the distribution of particle sizes of the ZnCr$_2$O$_4$/SiO$_2$ samples heated at 1000 and 1100 °C, CdCr$_2$O$_4$/SiO$_2$ sample heated at 1100 °C, CoCr$_2$O$_4$/SiO$_2$ samples heated at 1000 and 1100 °C, and the CuCr$_2$O$_4$/SiO$_2$ sample heated at 1000 °C.
C. IR and Raman Spectroscopy

The vibrational spectra of ACr$_2$O$_4$/SiO$_2$ (A = Zn, Cu, Cd, Co) nanocomposites were studied for the first time. The nanocomposites with highest chromite content (according to PXRD results) were selected for this study, namely the ZnCr$_2$O$_4$/SiO$_2$-1100°C, CuCr$_2$O$_4$/SiO$_2$-1000°C, CoCr$_2$O$_4$/SiO$_2$-1100°C and CdCr$_2$O$_4$/SiO$_2$-1200°C samples. The spectra recorded at room temperature are depicted in Fig. 3 (Raman spectra) and observed maxima are presented in Table II. The assignment of the observed bands (see Table II) reflects previous papers concerning the vibrational spectra of transition metals chromites [26]–[33]. This assignment is based on chromites belonging to the normal cubic II-III spinels with space group $Fd-3m$ ($O_n^3$) for which group theoretical treatment yields following vibrational representations:

$$A_{1g} + E_g + F_g + 3F_{2g} + 2A_{2u} + 2F_{cu} + 4F_{1u} + 2F_{2u}.$$

The $A_{1g}$, $E_g$ and three $F_{2g}$ modes are Raman active while four $F_{1u}$ modes are IR active. The potential lowering of the cubic $O_h$ symmetry to tetragonal $D_{4h}$ symmetry, which can occur due to eventual Jahn-Teller effect, is connected with splitting of triple degenerate modes $F_{1u}$ (to $A_{2u}$ and $E_{u}$) and $F_{2g}$ (to $B_{2g}$ and $E_{g}$), and of doubly degenerate mode $E_g$ (to $A_{1g}$ and $B_{1g}$).

The vibrational manifestations of CoCr$_2$O$_4$/SiO$_2$ nanocomposites are fully in accord with the expected presence of cobalt chromite with cubic symmetry. Very similar is the situation concerning ZnCr$_2$O$_4$/SiO$_2$ nanocomposites with exception of the absence of the weak $E_g$ mode in the Raman spectra. The Raman spectra of the CdCr$_2$O$_4$/SiO$_2$ nanocomposites confirm the presence of cubic cadmium chromite in examined samples, as is consistent with the PXRD analysis. However; the recorded spectra were complicated by the presence of other nanocrystalline phases as chromium(III) oxide (bands at ca. 300, 350, 525, 550 and 610 cm$^{-1}$) and especially cristobalite (bands at ca. 225 and 410 cm$^{-1}$). The absence of $A_{1g}$ mode is in accord with its very low intensity in Raman spectrum of bulk CdCr$_2$O$_4$ crystals [17]. The infrared spectra of CdCr$_2$O$_4$/SiO$_2$ nanocomposites exhibit only strong absorption bands of the cristobalite phase.

The vibrational spectra of the CuCr$_2$O$_4$/SiO$_2$ nanocomposites contain much higher number of the CuCr$_2$O$_4$ modes compared to other prepared chromites. The similar character of the spectra was observed also for bulk CuCr$_2$O$_4$ samples [18] and can be explained by Jahn-Teller effect of Cu(II) ions leading to lowering of lattice symmetry [16]. The observed bands can be assigned to splitting of $F_{1u}$ (4) mode (IR bands at 116, 131 and 187 cm$^{-1}$), $F_{2g}$ (3) mode (Raman bands at 120 and 186 cm$^{-1}$), $F_{1u}$ (1) mode (IR bands at 568 and 608 cm$^{-1}$). The assignment of Raman bands in 400 - 560 cm$^{-1}$ region is complicated by the overlapping of splitted $F_{2g}$ (2) modes with $E_g$ modes, which is associated with the changes of bands intensity (probably in terms of new $A_{1g}$ mode formation). Expected splitting of IR active $F_{1u}$ (2) mode was not recorded due to strong absorption of silica matrix. Observed level of above-mentioned splitting of degenerate modes indicates most likely tetragonal symmetry of prepared copper chromite [18], which is consistent with the PXRD observation.

D. Magnetic Properties

Results of magnetic measurements of the single-phase chromite nanocomposites are shown in Fig. 4 and 5. For the Zn-containing nanocomposites annealed at 1000°C, the low-field magnetization, recorded in the zero field-cooled (ZFC) and field-cooled (FC) regime is almost identical. Both curves show a single anomaly at $T_N^* = 12.5$ K, which corresponds exactly to the Neél temperature of the bulk ZnCr$_2$O$_4$. The $T_N^*$ shows a negligible temperature shift ($T_N^* = 12.0$ K) with applied field of 5 T, in consistency with
The bulk CdCr$_2$O$_4$ orders antiferromagnetically at
is significantly different in comparison to the bulk material. (field-induced ferromagnetic state in high magnetic fields and undergoes several magnetic phase transitions to the
reduction of the $\theta$ temperature, $\theta$ is of Curie-Weiss character with the paramagnetic Curie magnetization of the CdCr$_2$O$_4$ nanocomposite shows a broad particle size of about 20 nm are not much modified. Zn-chromite nanocrystals embedded in the silica matrix with
removed. It is evident, that for the magnetic properties of the symmetry condition for the magnetic geometric frustration is
structure disorder, mostly in the nanoparticle shells, where the character of the magnetization isotherm recorded at 2 K cannot be simply explained, the best possible interpretation so far is the surface spin phenomenon as in case of the Zn-chromite nanocrystals embedded in the silica matrix with particle size of about 20 nm are not much modified.

The temperature dependence of the low-field ZFC magnetization of the CdCr$_2$O$_4$ nanocomposite shows a broad maximum at $\sim T_m = 60$ K, followed by a steep increase of the magnetization on cooling. The FC curve exhibits, on contrary, a paramagnetic-like trend and deviates from the ZFC curve at a irreversibility-like temperature $T_{irr} = 80$ K. The 1 T-curve is of Curie-Weiss character with the paramagnetic Curie temperature, $\theta_P \sim \sim -138$ K, which is considerably reduced in comparison to the bulk value, $\theta_{P bulk} = -380$ K. The observed reduction of the $\theta_P$ can be interpreted as a consequence of the structure disorder, mostly in the nanoparticle shells, where the symmetry condition for the magnetic geometric frustration is removed. It is evident, that for the magnetic properties of the Zn-chromite nanocrystals embedded in the silica matrix with particle size of about 20 nm are not much modified.

The assignment of the vibrational bands of the prepared transition metal chromite nanoparticles embedded in the silica matrix.

<table>
<thead>
<tr>
<th>Table II</th>
<th>The Assignment of the Vibrational Bands of the Prepared Transition Metal Chromite Nanoparticles Embedded in the Silica Matrix.</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>ZnO$_2$/SiO$_2$-1100 $^\circ$C</td>
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<tr>
<td>Raman (cm$^{-1}$)</td>
<td>FTIR (cm$^{-1}$)</td>
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<td>390 s</td>
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<td>703 s</td>
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* Abbreviation "n.o." denotes expected vibrational bands, which were not observed due to silica matrix.

For the CuCr$_2$O$_4$ nanocomposite, the temperature dependence of the low-field ZFC and FC magnetization, respectively bifurcate at $T_C = 150$ K, and additional broad maximum appears at $T_m \sim 30$ K, as demonstrated in the Fig. 5. The $T_C$ roughly corresponds to the ordering temperature of the bulk CuCr$_2$O$_4$, similarly as reported in MnCr$_2$O$_4$ nanoparticles [19], the ordering temperature can be enhanced with the size reduction. However, the two other anomalies are of unclear origin. The character of the 30 K-maximum on the ZFC curve resembles that of a superparamagnetic system with medium particle size distribution. The saturation of the low-field FC curve can be viewed as a superposition of the ferromagnetic-like component coming from the regular order (at the $T^{*} = 150$ K) and a component of the SPM fraction with inter-particle interaction, as the curve changes its slope roughly at 30 K. The temperature dependencies of the magnetization recorded at higher magnetic fields (not shown) show a steep increase at the $T_C$, however
the anomaly at 30 K is suppressed at 4 T. The observed paramagnetic Curie temperature, $\theta_P \sim -23$ K, estimated from the high-temperature part of the magnetic susceptibility, which contains contributions of the Cu and Cr sublattices, just signalizes, that the antiferromagnetic exchange path is dominant in the system. An additional minority feature can be observed at $\sim 100$ K on the low-field ZFC curve. It could be attributed to an additional order-to-order magnetic phase transition, however, there are no magnetization data available down to low temperatures on a bulk compound to support or exclude this interpretation. Moreover, the anomaly is completely suppressed in higher magnetic fields; therefore it can originate from a tiny amount of a magnetic impurity. The hysteresis loop recorded at 2 K shows a tiny necking, which can be interpreted as a superposition of the two phases with slightly different magnetic hardness. It closes at $\sim 3$ T, in consistency with the temperature dependence of magnetization, and the coercivity values is about 0.4 T at 2 K. This observation rather well support the fact, that part of the sample (potentially the core of the nanocrystals) behaves more-or-less like a bulk material, while the rest of the sample (the disordered shells of the nanocrystals) exhibit SPM-like phenomena modified by inter-particle interaction.

The temperature dependence of magnetization of the CoCr$_2$O$_4$ nanocomposite, shown in the Fig. 5, is characteristic with a series of anomalies at the temperatures almost corresponding to the bulk sample: $T_C = 99$ K and $T_S = 26$ K. The anomaly related to the so-called lock-in temperature ($T_f = 14$ K in bulk) [34] was not detected. A considerably large negative paramagnetic Curie temperature, $\theta_P \sim -86$ K, estimated form the high-temperature part of the magnetic susceptibility, was observed, pointing to AF interactions in the system. The hysteresis loop at 2 K (inset of the Fig. 5) shows a similar character as in case of the CuCr$_2$O$_4$, the coercivity is about 0.6 T. As evidenced by the obtained results, the behavior of the CoCr$_2$O$_4$ nanocrystals is not
much modified in comparison to the bulk material. It is in
consistence with the assumption, that collapse of the magnetic
order in the ground state magnetic phase is connected with size
reduction below the coherence length of the conical component
(∼ 3 nm), which is not the case in our sample. The lack of the
$T_f$-related anomaly can be, however, tentatively attributed to the
size effect; as this temperature corresponds to stabilization
significantly affects the crystallization of the amorphous silica


spinel phase is formed in the ZnCr$_2$O$_4$/SiO$_2$, CdCr$_2$O$_4$/SiO$_2$

C. At the zinc and cobalt samples remained the

ACKNOWLEDGMENT

The authors thank for financial support of the Grant Agency of the Czech Republic, the project no. P108/10/1250.

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