Synthesis and Magnetic Properties of CuCr$_{1.65}$Se$_4$ Nanoparticles

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CuCr$_{1.65}$Se$_4$ nanoparticles crystallize in the monoclinic Cr$_2$Se$_3$-type structure of the space group $I2/m$. The average crystalline size basis on the line broadening is less than 10 nm. With decrease of the size of grains a change from ferromagnetic to ferrimagnetic order, a lack of the magnetization saturation and a strong spin-orbit coupling visible in the large value of the Landé factor $g_\alpha = 2.72$ are observed. The change in magnetic order is caused by the change of the crystalline symmetry from the cubic phase to monoclinic one.

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1. Introduction

The chromium-based spinel chalcogenides, ACr$_2$X$_4$ ($A = Cu$, Cd, Hg, Fe, Co; $X = S$, Se, Te) [1] which are ferro/ferrimagnetic insulators, semiconductors or even metals display unique properties in the bulk [2, 3]. Some of them are used as example ferrites for a radio engineer-

In Fig. 1 there are visible diffraction lines of the Cu$_{1.96}$Cr$_2$Se$_4$ cubic phase ($Fd-3m$) and traces of pure selenium and chromium after 15 h of milling. In Fig. 2 the Cu$_{1.65}$Se$_4$ monoclinic phase ($I2/m$), type-Cr$_2$Se$_3$ with the basic lattice parameters: $a = 6.227$ Å, $b = 3.582$ Å, $c = 11.528$ Å and $\beta = 90.77^\circ$ was identified in all alloys after 30, 45, 60, 85, 110 and 135 h of milling. With increase of milling time the lattice parameters are slightly decreasing and the line broadening is changing as well. In case of the diffraction lines overlapping there is possible to estimate the average crystallite size bising on.
the line broadening. So, the mean crystallite sizes for as mixed powders are about: 40–60 nm after 15 h of milling, 30–40 nm after 30, 45, 60, 85 and 110 h of milling and less than 10 nm after 135 h of milling. Powders annealed at 900 °C (milled 45 h and 135 h) have estimate size of crystallites in a range of 20 nm.

\[ \text{µ}_{\text{eff}} \approx 4.97 \mu_B/\text{f.u.} \] for a high-spin Cr\(^{3+}\) \((S = 3/2, g = 2)\) is comparable with the effective number of the Bohr magnetons. This property means that the magnetic properties come mainly from the Cr\(^{3+}\) ions. The temperature dependence of the effective magnetic moment estimated from equation: \( \mu_{\text{eff}} = 2.83\sqrt{T} \) strongly depends on temperature. It shows both a broad maximum around the temperature of 170 K and a broad minimum close to room temperature. At the maximum \( \mu_{\text{eff}} \) is close to the spin-only value. Upon lowering the temperature \( \mu_{\text{eff}} \) gradually decreases from 4.77 \( \mu_B/\text{f.u.} \) at 170 K to 1.21 \( \mu_B/\text{f.u.} \) at 5 K (Fig. 6). This behaviour is also visible in the product of \( \chi T \) in Fig. 6. It can mean that the ferrimagnetic order dominates from one side and the strong magnetocrystalline anisotropy exists in the sample from the other. Also a strong spin–orbit coupling visible in the large value of the Landé factor \( g_\chi = 2.72 \) may exist, too. A superparamagnetism was not stated in the CuCr\(_{1.65}\)Se\(_4\) nanoparticles since the magnetization curves were deviated from the universal function of magnetization vs. magnetic field divided by the temperature [13].

### Table I

<table>
<thead>
<tr>
<th>C</th>
<th>θ</th>
<th>( T_C )</th>
<th>( \mu_{\text{eff}} )</th>
<th>( \rho_{\text{eff}} )</th>
<th>( g_\chi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.461</td>
<td>225</td>
<td>173</td>
<td>5.265</td>
<td>4.975</td>
<td>2.72</td>
</tr>
</tbody>
</table>

Fig. 3. Magnetic susceptibility \( \chi \) vs. temperature \( T \). The solid (olive) line, \( C/(T - \theta) \), is for an estimation of the Landé factor from the Curie constant. The solid (black) line, \((T - \theta)/C\), indicates a Curie-Weiss behavior.
Fig. 4. Magnetization $M$ vs. magnetic field $H$ at 5 and 350 K.

Fig. 5. Hysteresis loops at 5 and 350 K.

Fig. 6. Product $\chi T$ and effective magnetic moment $\mu_{\text{eff}}$ vs. temperature $T$.

4. Conclusions

The results of CuCr$_{1.65}$Se$_4$ nanoparticles mentioned above suggest that the decrease of the size of grains causes a change both from cubic to monoclinic phase and from ferromagnetic order to ferrimagnetic one. In consequence a lack of the magnetization saturation and a strong spin–orbit coupling visible in the large value of the Landé factor $g_\chi = 2.72$ are observed.

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References