ABSTRACT: A facile synthesis approach for the synthesis of ternary intermetallic nanocrystals was demonstrated exemplarily with the Heusler compound Co$_2$FeGa. The method, involving prefabricated multilwalled carbon nanotubes which act as a template and protective shell, results in the formation of mainly spherical, chemically stable, and crystalline nanoparticles with a well-defined diameter distribution. As an example, for novel functionalities arising from downscaling a bulk material, we observe an enhancement of the coercive field of the Co$_2$FeGa nanocrystals by a factor of $\approx 30$. Our work can facilitate the exploration and eventually the tuning of physical properties of ternary and other intermetallic compounds at the nanoscale.

Heusler materials are a family of intermetallic compounds with the general stoichiometry of X$_2$YZ, where X and Y denote transition metals and Z a main group metal. They are named after Friedrich Heusler who discovered ferromagnetism in the compound Cu$_2$MnAl$^{1,2}$ Nowadays more than 1300 Heusler compounds are reported in literature and their known physical properties extend well beyond the different types of magnetism and comprise, among others, magnetocaloric, thermoelastic, shape memory, half-metallic ferromagnetic, superconducting, semiconducting, and potentially topologically insulating materials.$^3$ Heusler materials are usually prepared as single or polycrystalline bulk materials or thin films. However, for numerous potential applications (e.g., in spintronics), the nanoscale dimensions of a material cannot be neglected.$^4$ When the characteristic length of a material is in the range of nanometers, finite size effects and a high surface to volume ratio strongly affect the physical properties of a material. Examples for such occurrences are ballistic transport in carbon nanotubes,$^5$ photoluminescence of gold nanoparticles,$^6$ or the enhanced catalytic activity of nanoparticles.$^7$ In order to investigate the effects of downscaling on a given compound, crystalline samples with nanoscale dimensions (e.g., in the form of nanoparticles or nanowires) are necessary.

A straightforward way of preparing Heusler nanoparticles is ball milling of polycrystalline starting materials.$^8-10$ This process, however, is rather crude as it involves high-energy input on debris of the milled material, which may lead to structural changes. Further, Heusler particles which are prepared this way are prone to oxidation and in this sense require very careful handling. A recent approach to synthesize Heusler nanoparticles was presented by L. Basit and co-workers.$^{11}$ They applied a wet chemical method which involved the precipitation of Heusler particles on a porous silica matrix. Although this method avoids the known issue of the high kinetic energies involved in ball milling processes, the control of the particle size remains poor and the synthesis requires an additional coating step to protect the nanoparticles from oxidation, which is further followed by HF etching to retrieve the particles from the silica matrix. With such drawbacks in the synthesis, the study of the physical properties of Heusler nanoparticles in a reliable manner constitutes a challenge.

In order to help overcome the limitations of the known synthesis methods, we suggest an alternative and elegant approach based on nanoparticles encapsulated inside the hollow cavity of carbon nanotubes. In our experiments, we have filled multiwall carbon nanotubes with the intermetallic Heusler compound Co$_2$FeGa, by extending a reported solution-filling approach for carbon nanotubes.$^{12}$

We investigated the geometry of the filling particles and their position in respect to the carbon nanotubes with scanning electron microscopy (SEM) (Figure 1) and transmission electron microscopy (TEM). The distribution of filling particle diameters ($d_{nano} = 35 \pm 7$ nm) measured perpendicular to the long axis of the tubes coincides with the distribution of the inner diameter of filled carbon nanotubes ($d_{CNT} = 38 \pm 9$ nm) (Figure 2). Thus, we observe that the confinement of the intermetallic material to the inner diameter of the nanotubes allows control of the particle size.

The aspect ratio (i.e., the ratio of the long particle axis to its short axis) of the majority of the filling particles (86%) is spherical within one standard deviation in a sample of 70 filling...
particles (Figure 3). Only about 5% of the particles show an aspect ratio larger than 1.5, where 1.9 constitutes the largest aspect ratio found in our samples. We attribute the primary formation of spherical particles to the minimization of surface energies during the formation of particles in the reduction process.

The samples have been exposed to air for several months; however, we find no hints for oxidation of the filling particles, even at those close to the open tips of the carbon nanotubes. This chemical stability is a significant advantage, not only over unprotected intermetallic nanoparticles, but also over Heusler thin films and bulk Heusler compounds, where battling oxidation constitutes a permanent challenge.13,14

We observe particles inside nanotubes positioned at varying places along the tube: they occur in the middle of tubes, as well as at the tip and in between (see Figure 1). Our samples show no significant amount of particles outside of carbon nanotubes. The virtual absence of outside particles is confirmed by thermogravimetric analysis (TGA): here, we observe a weight loss contributed to the combustion of carbon nanotubes (Figure 3) and no additional features in the data curve. In contrast to our here discussed samples, other samples of filled carbon nanotubes with numerous outside particles (confirmed with SEM and TEM), exhibit an increase in mass prior to the combustion of the carbon nanotubes (Figure 4). We attribute this increase to the oxidation of the outside particles that are no longer protected against oxidation by the contact to the outer carbon shells of the nanotubes due to the applied elevated temperature. The observation, that this specific increase in mass is not present in the here discussed samples of filled carbon nanotubes, further evidences the high sample purity. From the TGA data, we also derive a filling yield of intermetallic material of approximately 2−3 wt %, which, in a rough estimation, corresponds to 40−50% filling efficiency in respect to the theoretical limit.

Concerning the formation of the observed well-separated nanoparticles aligned along the inner cavity of the carbon nanotubes (Figure 1), we suggest the following mechanism (Figure 5): (a) The starting materials dissolved in a solvent...
TEM-based nanobeam electron diffraction carried out on individual Heusler nanoparticles reveals that the filling particles are single crystalline (Figure 6). We observe the Heusler-typical L2₁ lattice structure, as indicated by the superstructure reflections corresponding to the 111 and 200 lattice planes, which coincides with the bulk one, giving evidence for a high structural integrity of the filling particles. The L2₁ structure of the Heusler nanoparticles points to an absence of atomic site disorder within the filling particles, which we attribute to the moderate temperatures applied during synthesis. Hence, our synthesis approach may constitute a promising way to produce Heusler materials with high crystalline integrity, while suppressing atomic site disorder.

In order to investigate the physical effects of downsizing, we exemplarily studied the magnetic properties of the encapsulated Heusler nanoparticles by performing field- and temperature-dependent measurements of the magnetization (Figure 7). The saturation magnetic moment is \( m_s = 4.5 \pm 0.6 \, \mu B/\text{f.u.} \), a value which is comparable to the experimental values reported for Co₂FeGa bulk samples (4.72 \( \mu B/\text{f.u.} \leq m_{s,\text{exp}} \leq 5.15 \, \mu B/\text{f.u.} \)).16–18 The temperature dependence shows that the saturation magnetization of the sample changes less than 5% when going from 5 to 300 K. The weak decrease of the magnetic moment with rising temperature in the above-mentioned temperature range correlates with the known high \( T_C \) for bulk Co₂FeGa15,16 and indicates that two important magnetic properties of the bulk material, the large saturation magnetization and high critical temperature, are preserved in the Heusler nanoparticles. This result is contrasted by a pronounced concomitant change in magnetic hardness. The measured coercive field of the Co₂FeGa nanoparticles is \( H_C = 46.6 \pm 0.7 \, \text{kA/m} \) (approximately 585 Oe), which is more than a factor of 30 larger than the measured coercive field \( H_C = 1.5 \, \text{kA/m} \) (approximately 19 Oe) of a polycrystalline bulk Co₂FeGa reference sample, which had been prepared from elemental metals by the use of the arc-melting technique, as described elsewhere.19 The large enhancement of the coercive
Heusler-measured hysteresis loops at 5 K and at 300 K. Nanoparticles at room temperature, as is clearly seen from the ferromagnetic and not yet superparamagnetic character of the particles in a well-defined method based on altered magnetic properties of Co2FeGa nanoparticles due to disorder but also to scale a given intermetallic compound crystalline Heusler (nano)materials with low atomic site size reduction of the material. Our approach opens the form of chemically stable and spherical nanoparticles with compounds but also numerous other intermetallic materials in size reduction of the material. Our approach opens the form of chemically stable and spherical nanoparticles with compounds but also numerous other intermetallic materials in.

Figure 7. Hysteresis curves of carbon nanotubes filled with Co2FeGa Heusler nanoparticles measured at 5 K and 300 K. The lower panel shows an enlarged view on the hysteresis curve in comparison with a polycrystalline bulk sample. Here, the enhanced coercive field in Heusler-filled carbon nanotubes can be clearly identified.

In summary, our study demonstrates that a wet chemical method based on filling carbon nanotubes with nitrate solutions offers a facile way to synthesize ternary intermetallic nanoparticles in a well-defined manner. We exemplarily observed altered magnetic properties of Co2FeGa nanoparticles due to size reduction of the material. Our approach opens the perspective of investigating the properties of not only Heusler compounds but also numerous other intermetallic materials in the form of chemically stable and spherical nanoparticles with well-defined dimensions. The here reported synthesis approach may constitute an exceptional way not only to synthesize single crystals Heusler (nano)materials with low atomic site disorder but also to scale a given intermetallic compound down to nanosize.

■ ASSOCIATED CONTENT

2 Supporting Information
Experimental and measurement details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ REFERENCES


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Notes
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