



Hydrogenation studies on NdScSi and NdScGe

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ABSTRACT

NdScSi and NdScGe were synthesized from the elements via arc-melting and subsequent annealing. Their ordered La₂Sb type structures, with space group *I4/mmm*, were refined from single crystal X-ray diffractometer data: $a=428.94(6)$ and $b=1570.5(3)$ pm, $wR2=0.0395$, 309 F^2 values for NdScSi and $a=431.2(1)$ and $c=1581.3(5)$ pm, $wR2=0.1220$, 227 F^2 values for NdScGe, with 11 variables per refinement.

Hydrogen insertion was performed on both Nd-based intermetallics by solid/gas reaction. Hydrogen uptake keeps the pristine compound space group but yields an anisotropic expansion of the unit cell with a large increase of c ($\approx +7\%$) and a slight decrease of a ($\approx -1.7\%$) parameters. Hydrogen absorption at 350 °C and under 5 bar of H₂ pressure shows that the hydride NdScSiH_{1.48(5)} is formed. An *in-situ* neutron diffraction study during the deuteration of NdScSi reveals for the first time in a CeScSi-type compound, the possibility to fill two interstitial sites with deuterium atoms, leading to the composition NdScSiD_{1.5} for the deuteride adopting then the La₂Fe₂Se₂O₃-type structure.

From magnetization measurements, we evidence that hydrogenation strongly reduces the Curie temperature of NdScSi ($T_C=175$ K) and NdScGe ($T_C=194$ K) since NdScSiH_{1.5} and NdScGeH_x undergo a magnetic transition at 4 K and around 2 K, respectively.

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1. Introduction

The tetragonal La₂Sb structure [1] is one of the basic structure types for intermetallic compounds [2]. Besides the binary series of RE₂Sb antimonides and RE₂Bi bismutides (RE=rare earth element), a larger variety of ternary rare earth-containing representatives of this structure are known, e.g. the series of REscSi silicides [3], REscGe germanides [4], and REscSb antimonides [5]. The distinctly smaller size of scandium allows for a complete ordering of the two rare earth sites leading to the formation of the CeScSi-type structure. Substitution of the antimony by the tetravalent silicon and germanium permits for a certain electronic flexibility.

The silicides and germanides have been intensively studied with respect to their magnetic properties since several representatives exhibit comparatively high magnetic ordering temperatures: $T_N=26$ and 43 K for CeScSi and CeScGe [6–9], the 194 K ferromagnet NdScGe [10] or ferromagnetic TbScGe ($T_C=216$ K) [11]. The Curie temperatures of GdScSi (354 K) and GdScGe (349 K) are even above room temperature and both compounds show a

moderate magnetocaloric effect [12].

Besides the high magnetic ordering temperature, the interest in the REscSi and REscGe compounds concerns their hydrogenation behavior. The larger rare earth atoms form layers of condensed tetrahedra that can be filled with hydrogen leading to the quaternary compounds REscSiH and REscGeH in compliance with the many ZrCuSiAs-type phases [13–15]. The hydrogen insertion has a drastic influence on the magnetic ground state. Recent examples are the pairs CeScSi/CeScSiH [16] and GdScGe/GdScGeH [17]. In both cases hydrogenation leads to a drastic decrease of the magnetic ordering temperature: (i) T_N decreases from 26 to 3 K from CeScSi to CeScSiH and (ii) the 350 K ferromagnet GdScGe switch to the 6 K antiferromagnet GdScGeH.

Based on these striking results we extended our systematic studies on the pairs of REscSi/REscSiH and REscGe/REscGeH compounds with respect to the neodymium representatives. So far, the ternaries have only been studied on the basis of powder diffraction data [3,4,10,18]. Herein we report on single crystal X-ray diffraction data for the precursor compounds NdScSi and NdScGe and hydrogenation/deuteration experiments with respect to changes in the magnetic ground state. In particular, we present *in-situ* neutron diffraction experiments of deuteration which evidence a new structural type of deuteride obtained from CeScSi-type compounds.

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2. Experimental

2.1. Synthesis

Starting materials for the preparation of the NdScSi and NdScGe samples were neodymium ingots (Johnson-Matthey), scandium ingots (Johnson Matthey), silicon and germanium lumps (Alfa Aesar), all with stated purities higher than 99.9%. For NdScGe, the elements were weighed in the ideal 1:1:1 atomic ratio and arc-melted [19] three times under *ca.* 700 mbar argon pressure. Argon was purified with titanium sponge (900 K), silica gel, and molecular sieves. The arc-melted button was subsequently sealed in an evacuated silica tube and annealed at 1173 K for 14 days. For preparation of the NdScSi sample the starting composition was 0.95:1.05:1 in order to avoid formation of the Nd_{2-x}Sc_{3+x}Si₄ phase. After the arc-melting procedure the sample was annealed for a longer period, *i. e.* three weeks, at 1173 K. The resulting silvery ingots were stable in air over weeks.

Preliminary hydrogenation experiments were performed by solid-gas reaction in a stainless steel container hermetically sealed with a graphite joint. The annealed ingots were crushed and heated under vacuum at temperatures between 250 and 350 °C for 2 h and then exposed to 30 bar of hydrogen gas at the same temperature for 1.5 days. Indeed, below 250 °C residual pristine compound is still present and above 350 °C the container becomes no longer tight. The formed hydrides are stable in air.

Further hydrogen sorption kinetics were investigated by the use of an automatic sievert-type volumetric apparatus (HERA, hydrogen storage system) in the temperature range from 200 to 350 °C and with 5 bar of H₂ [20].

2.2. Scanning electron microscopy

The NdScSi and NdScGe crystals investigated on the diffractometers were studied by EDX using a Zeiss EVO MA10 scanning electron microscope with NdF₃, Sc, SiO₂, and Ge as standards for the semiquantitative measurements. No impurity elements have been detected. The conchoidal fracture of the crystals hampered quantitative analyses.

2.3. X-ray powder and single crystal data

The polycrystalline NdScSi and NdScGe samples were characterized through Guinier powder patterns (imaging plate technique, Fujifilm BAS-1800) with CuK α ₁ radiation and α -quartz (*a*=491.30 and *c*=540.46 pm) as an internal standard. The tetragonal lattice parameters (Table 1) were refined from the powder diffraction data by a least-squares routine. Correct indexing of the patterns was ensured by intensity calculations [21] using the atomic parameters obtained from the structure refinements. Our data are in agreement with earlier literature results on NdScSi and NdScGe powders [3,4]. The hydride samples were analyzed with a Philips1050-diffractometer (CuK α radiation) and their cell parameters were determined by a full-pattern matching of the X-ray diffractogram using the Fullprof program [22].

Irregularly-shaped single crystals of NdScSi and NdScGe were selected from the crushed annealed samples and glued to thin quartz fibers. They were first investigated by Laue photographs on a Buerger camera (white molybdenum radiation, Fuji-film image plate technique) in order to check their quality for intensity data collection. The NdScSi data set was collected at room temperature by use of a four-circle diffractometer (CAD4) with graphite monochromatized MoK α radiation and a scintillation counter with pulse height discrimination. Scans were taken in the $\omega/2\theta$ mode. An empirical absorption correction was applied on the basis of Ψ -scan data, accompanied by spherical absorption corrections.

Table 1

Crystal data and structure refinement results of NdScSi and NdScGe with ordered La₂Sb type structure; space group *I4/mmm*; *Z*=4.

| Compound | NdScSi | NdScGe |
|--|----------------|------------------|
| <i>a</i> , pm | 428.94(6) | 431.2(1) |
| <i>c</i> , pm | 1570.5(3) | 1581.3(5) |
| <i>V</i> , nm ³ | 0.2890 | 0.2940 |
| Molar mass, g mol ⁻¹ | 217.29 | 261.79 |
| Calculated density, g cm ⁻³ | 5.00 | 5.91 |
| Absorption coefficient, mm ⁻¹ | 20.2 | 29.4 |
| Diffractometer | CAD4 | IPDS2 |
| Detector distance, mm | – | 60 |
| Exposure time, min | – | 30 |
| ω range; increment, deg. | – | 0–180, 1.0 |
| Integr. param. <i>A</i> , <i>B</i> , EMS | – | 12.5; 2.5; 0.010 |
| <i>F</i> (000), e | 380 | 452 |
| Crystal size, μ m ³ | 20 × 20 × 30 | 10 × 20 × 20 |
| Transm. ratio (max/min) | 1.57 | 2.04 |
| θ range, deg. | 2–40 | 4–35 |
| Range in <i>hkl</i> | ± 7, ± 7, ± 28 | ± 6, ± 6, ± 25 |
| Total no. reflections | 3564 | 2009 |
| Independent reflections/ <i>R</i> _{int} | 309/0.0662 | 227/0.1921 |
| Reflections with <i>I</i> ≥ 2 σ (<i>I</i>)/ <i>R</i> _{σ} | 298/0.0240 | 164/0.1011 |
| Data/parameters | 309/11 | 227/11 |
| Goodness-of-fit on <i>F</i> ² | 1.083 | 1.088 |
| <i>R</i> ₁ / <i>wR</i> ₂ for <i>I</i> ≥ 2 σ (<i>I</i>) | 0.0172/0.0389 | 0.0574/0.1101 |
| <i>R</i> ₁ / <i>wR</i> ₂ for all data | 0.0184/0.0395 | 0.0936/0.1220 |
| Extinction coefficient | 0.0031(6) | 0.004(2) |
| Largest diff. peak /hole, e Å ⁻³ | 1.84/–2.30 | 2.78/–2.72 |

Intensity data of the NdScGe crystal were collected at room temperature by use of a Stoe IPDS-II imaging plate diffractometer in oscillation mode (graphite monochromatized MoK α radiation). A numerical absorption correction was applied to the data set. All relevant crystallographic data and details of the data collections and evaluations are listed in Table 1.

The Guinier patterns of the NdScSi and NdScGe samples clearly indicated isotypism with the respective cerium compounds [16]. Analyses of the two data sets were in agreement with space group *I4/mmm* and the positional parameters of CeScSi [16] were taken as starting values. Both structures were then refined with SHELXL-97 [23,24] (full matrix least squares on *F*_o²) with anisotropic displacement parameters for all sites. The occupancy parameters have been refined in a separate series of least squares cycles. All sites were fully occupied within two standard deviations. Final difference Fourier synthesis revealed no significant residual peaks. The refined atomic parameters and interatomic distances are listed in Tables 2 and 3. For NdScGe we find excellent agreement with a recent neutron diffraction study [10].

Further details on the structure refinements are available. Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No's. CSD-427369 (NdScSi) and CSD-427370 (NdScGe).

2.4. Neutron diffraction experiments

In-situ neutron powder diffraction experiments of deuteration were performed on the C2 diffractometer at the Canadian Neutron Beam Centre (CNBC), using a wavelength of λ =1.328 Å (Si(531) monochromator). C2 is equipped with a curved 800-wire BF₃ position sensitive detector with a wire spacing of 0.1°. The experimental setup is designed so that the sample holder can be filled with hydrogen/deuterium gas up to 40 bar and heated in the 25–400 °C temperature range [25]. The FullProf Suite program was used for nuclear structure refinements using the Rietveld method [22].

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