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NdNiMg$_5$, a New Magnesium-Rich Phase with an Unusual Structural Type

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Ⓢ *Supporting Information*

ABSTRACT: The new intermetallic NdNiMg$_5$ was discovered during the study of the Mg-rich part of the Mg−Nd−Ni system. It was synthetized by melting of the constituent elements in a sealed tantalum tube with subsequent annealing. Its structure was determined by X-ray diffraction on a single crystal. Crystal data: orthorhombic system, $Cmcm$, $Z = 4$, $a = 4.4799(2)$ Å, $b = 9.9827(3)$ Å, $c = 13.7854(10)$ Å, $d_{calc} = 3.49$ g·cm^{-3}. Its structure is made of infinite layers of Mg atoms that form blocks stacked along the c axis. These blocks, with a close-packed array of Mg atoms, are separated by infinite NiNd layers and connected through short Mg−Mg bonds. In the NiNd layer, the Ni and Nd atoms form an ordered graphite-type network. Antiferromagnetic ordering is observed with $T_N = 12$ K, and the effective magnetic moment μ_{eff} is equal to 3.89(1) μ_B.

The study of the Mg-rich part of a RE−TM−Mg ternary diagram (RE = rare earth and TM = transition metal) is of great interest for several practical applications and usually leads to the discovery of new interesting phases. For instance, the Mg-rich part of the Mg−Zn−RE system was studied to find new light structural materials with good corrosion resistance.[1−3] Long-period stacking/order (LPSO) phases with hexagonal close-packing (hcp) blocks of Mg were observed.[2,3] Face-centered-cubic (fcc) blocks made of Mg, Zn, and Y atoms were located between them. Many studies were also performed to find new candidates for solid hydrogen storage because of the low weight and cost of magnesium.[4−9] Only a few Mg-rich phases were reported in the literature, and to our knowledge, LaCuMg$_4$ is the richest fully ordered phase.[5] On the contrary, the structure of LaCuMg$_8$[7] is a strongly disordered derivative of the binary La$_2$Mg$_{17}$, and Gd$_{13}$Ni$_9$Mg$_{78}$[9] exhibits a complex structure that is not yet fully determined but seems to be partially disordered. Even if most of the ternary diagram RE−TM−Mg were studied in the past, we demonstrated that new careful and extended studies allow one to discover new phases.[7,9] The system Mg−Ni−Nd was chosen because of the promising results obtained on the hydrogen-storage properties of amorphous alloys.[6]

The new NdNiMg$_5$ phase was discovered during the study of the Mg-rich part of the Mg−Nd−Ni system using an electron probe microanalyzer with nominal composition NdNiMg$_8$.[10] This starting composition was chosen because of the previous discovery of the new phase LaCuMg$_8$.[7] For synthesis of the title compound, the metal pieces were enclosed in a sealed tantalum tube and melted in a high-frequency furnace. The tantalum tube was then enclosed in an evacuated quartz tube and annealed at 973 K for 10 days. The temperature was decreased to 300 K at 6 K·h^{-1}.[11] Unknown secondary phases were observed, and then other closed starting composition and annealing procedures were tested to reduce the amount of secondary phases.

Despite the inevitable presence of minor secondary phases that are different in amount and nature depending on the experimental procedure, the magnetic transition at 12 K is systematically evidenced by magnetic or resistivity measurements. The full pattern matching of the powder pattern of the sample used for magnetic measurements (see below) is shown in the Supporting Information. The study of the secondary phases is under progress.

The structure of NdNiMg$_5$ is made of infinite layers of Mg that form blocks stacked along the c axis (Figure 1).[12,13] These blocks are separated by NiNd layers and connected through short Mg−Mg bonds (drawn in red in Figure 1). The Mg blocks are made of a close-packed array of Mg atoms with Mg−Mg distances ranging from 3.108 to 3.223 Å. These distances are close to the average Mg−Mg distance of 3.203 Å in the Mg metal.[14] The connectivity of the empty [Mg$_4$] tetrahedra and [Mg$_6$] octahedra corresponds

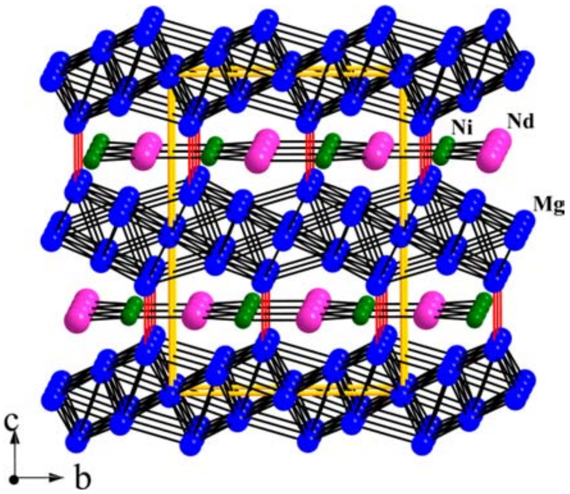

Figure 1. View along the a axis of the structure of NdNiMg$_5$. The Mg−Mg and Ni−Nd bonds are drawn.

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to the one observed in the fcc structure. The $[Mg_6]$ octahedra are sharing faces with the $[Mg_4]$ tetrahedra, which form double-edge-sharing chains (Figure 2a). The average distances between the center of the T_d or O_h interstitial sites and the Mg neighboring atoms are equal to 1.94 and 2.24 Å, respectively. These values are nearly equal to the ideal ones expected for a fcc stacking, i.e., $(1.5^{1/2})r_{Mg}$ and $\sqrt{2}r_{Mg}$ with r_{Mg} = 1.60 Å. Following this discussion, it can be assumed that the Mg atoms form a metallic network. The Ni and Nd atoms form an ordered graphite-type network (Figure 2b). Two rather different Ni−Nd distances are observed. The largest one, equal to 3.109 Å, is close to the sum of the metallic radii $r_{Nd} + r_{Ni} = 1.82 + 1.25 = 3.07$ Å,[15] whereas the shortest one, equal to 2.836 Å, is close to the sum of the covalent radii $r_{Nd} + r_{Ni} = 1.64 + 1.15 = 2.79$ Å.[16] The covalent character of the Nd−Ni bonding is in complete agreement with the low dimensionality of the Nd−Ni network. The Ni atoms are surrounded by six Mg atoms (Figure 3) with Ni−Mg distances equal to 2.668−2.804 Å, which are slightly shorter than the sum of the covalent (i.e., 2.75 Å) and metallic (2.85 Å) radii, respectively. The shortest Nd−Ni distance is comparable to the average distance of 2.68 Å observed in Mg_2Ni.[17] Considering a Nd−Mg distance of up to 3.4 Å, i.e., the sum of the metallic radii, there are 10 Mg atoms in the coordination sphere of Nd (Figure 3). The shortest Nd−Mg distance equal to 3.292 Å for the Mg1 position is similar to the shortest distance observed in Mg_3Nd.[18] If such hexagonal layers are already observed in other structures, for instance, in the ZrBeSi type,[19] the peculiarity in this case is that the magnetic REs belong to the hexagonal planes.

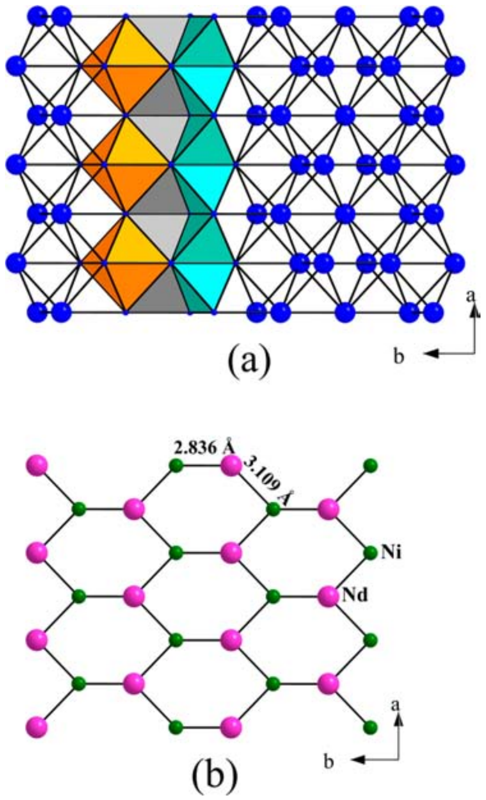

Figure 2. (a) View of one Mg block with some empty octahedra drawn in orange and tetrahedra in gray or cyan. (b) View of the NiNd layers along the c axis.

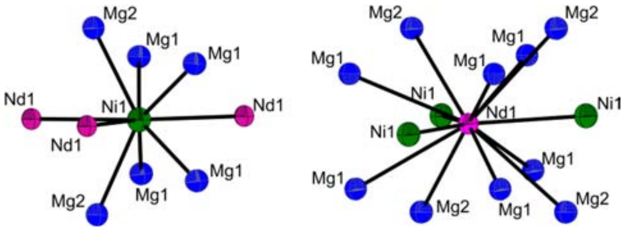

Figure 3. Environment of the Ni1 and Nd1 positions with 90% probability ellipsoids.

The distance between two consecutive NiNd layers is equal to 6.893 Å (i.e., $c/2$). One can also notice that despite the layered character of this structure a high density of 3.50 g·cm^{-3} is observed. This may be explained by the high compactness of the Mg blocks, which are connected through very short Mg−Mg distances, and the space between these blocks is filled by Nd and Ni atoms.

As explained in the introduction, only a few ternary Mg-rich ordered compounds are reported in the literature. $NdNiMg_5$ is, to our knowledge, the richest one. The structures of the richest phases are often disordered and derive from those of the corresponding binary compounds such as observed for $LaCuMg_8$[7] or $LaAg_{1.44}Mg_{10.56}$.[20] $LaCuMg_8$ crystallizes with the La_2Mg_{17}-type structure, and its formula can be rewritten as $(La_{1.74}Cu_{0.25})(Mg_{15.73}Cu_{1.28})$, which corresponds to the general formula $(La_{1-x}Cu_x)_2(Mg_{1-y}Cu_y)_{17}$. This close structural relationship explains the similarity of its hydrogen-absorption properties with those of La_2Mg_{17}.[8] The structure of $LaAg_{1.44}Mg_{10.56}$ is strongly related to the $ThMn_{12}$ structure type[20] with a Mg/Ag mixing on some crystallographic positions. The structures of the LPSO phases[2,3] are long-period stacking variants of the hcp structure of pure Mg. In the stacking sequence, fcc blocks are observed in which RE and Zn atoms are located. The degree of disorder inside the latter blocks is strongly dependent on the overall stoichiometry.[3]

As shown in the inset of Figure 4, the temperature dependence of the reciprocal magnetic susceptibility X_m^{-1} versus temperature follows a Curie−Weiss law above 130 K, with negative Curie−Weiss temperatures, $\theta_p = -16$ K, thereby indicating predominantly antiferromagnetic interactions.[21]

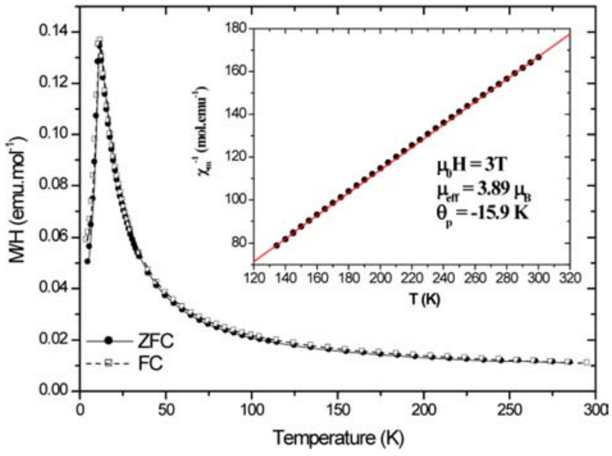

Figure 4. Temperature dependence of the magnetization M measured under an applied magnetic field $\mu_0 H = 0.05$ T determined in the zero-field-cooling (ZFC) and field-cooling (FC) processes. The inset displays the reciprocal susceptibility measured under an applied magnetic field $\mu_0 H = 3$ T with a Curie−Weiss fit (red line).

The experimental effective magnetic moment μ_{eff} calculated is 3.89(1) μ_{B}. The main contribution to magnetism is expected to arise from the RE. Because the 5d and 6s electrons are delocalized, the contribution of the RE to magnetism originates from the localized 4f electrons. The theoretical effective magnetic moment expected for Nd is then $\mu_{\text{eff}}^{\text{th}} = g_J[J(J+1)]^{1/2}\mu_{\text{B}} = 3.62$ μ_{B} ($4f^3$ configuration with $S = {}^3/_2$, $L = 6$, $J = {}^9/_2$, and $g_J = {}^8/_{11}$). The experimental value is slightly higher, and this may be attributed to (i) a small magnetic moment carried by Ni atoms, suggesting that their 3d bands are not completely filled, (ii) a contribution from conduction electrons, and (iii) the presence of a secondary phase. Neutron experiments are planned to address this question. Magnetization data were taken while the sample was being warmed. In a first step, the sample was prior cooled by zero field cooling (ZFC), and in a second step, it was prior cooled by applied field cooling (FC). Nevertheless, in both cases, the results are the same, and both M/H versus T curves are superposed (Figure 4). A cusplike behavior indicating antiferromagnetic ordering is clearly seen with a Néel temperature $T_{\text{N}} = 12$ K. Complementary physical characterizations are also in progress: magnetization versus field, specific heat, transport, and mechanical properties measurements.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format, table with interatomic distances, and an X-ray diffraction pattern. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(10) The composition of the phases in the sample was checked by microprobe analysis using a Cameca SX-100 instrument. Analysis was performed on the basis of intensity measurements of the Nd Lα, Ni Kα, and Mg Kα X-ray emission lines, which were compared with those obtained for the high-purity elements Nd, Ni, and Mg used as reference compounds.

(11) Starting materials for preparation of the samples were neodymium pieces (ZLX Tech, >99.9%), a nickel rod (Strem Chemicals, >99.9%), and a magnesium rod (Alpha Aesar, >99.8%).

(12) Crystal data: orthorhombic system, *Cmcm*, $Z = 4$, $a = 4.4799(2)$ Å, $b = 9.9827(3)$ Å, $c = 13.7854(10)$ Å, $d_{\text{calc}} = 3.49$ g·cm^{-3}. The refinement of the crystal structure was made using single-crystal X-ray diffraction data. The single crystal was isolated from a crushed block and selected by optical microscopy. Reflection data were collected at room temperature on an Enraf-Nonius Kappa CCD using Mo Kα radiation. A Gaussian-type absorption correction was applied, with the shape of the single crystal being determined with the video microscope of the diffractometer. A total of 2181 reflections were measured up to $\theta = 30°$. Data processing and all refinements were performed with the *Jana2006* program package.[22] All of the atom positions were located using the *SUPERFLIP* program.[23] At the end of the refinement, the reliability factors were $R[F^2 > 2\sigma(F^2)] = 0.021$ and $R_w(F^2) = 0.056$. $S = 1.34$ for 26 parameters, 516 independent reflections, and with a residual electron density in the range of −0.95 to +0.63 e·A^{-3}. The CIF file has also been deposited in the Fachinformationszentrum Karlsruhe (FIZ; 76344 Eggenstein-Leopoldshafen, Germany) as reference CSD 426469.

(13) The atomic positions are Nd1 [$^1/_2$, 0.10948(3), $^1/_4$], Ni1 [0, 0.32540(8), $^1/_4$], Mg1 [$^1/_2$, 0.40310(14), 0.14140(12)], Mg2 [0, 0.20670(13), 0.07662(11)], and Mg3 ($^1/_2$, 0, 0).

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(21) Magnetic susceptibility measurements were carried out with a Quantum Design SQUID magnetometer on a small block of 40.0 mg. The experimental conditions are given in the legend of Figure 4.

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■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on November 13, 2013, with a minor text error in the Abstract. The corrected version was reposted on the same day.