Crystal Growth and Magnetic properties of RMg₃ (R = La, Ce and Nd)

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Abstract. We have successfully grown the single crystals of RMg₃ (R = La, Ce and Nd) compounds by Bridgman method, in a sealed molybdenum crucible. These compounds crystallize in the cubic BiF₃-type structure with the space group Fm̅3m. The powder x-ray diffraction pattern clearly revealed that the samples were single phase without any impurity. The crystals were oriented by means of Laue back reflection method for the magnetic and transport measurements. It has been found that CeMg₃ orders antiferromagnetically at \( T_N = 2.6 \) K, while NdMg₃ shows two magnetic orderings with \( T_{N1} = 6.8 \) K and \( T_{N2} = 2.8 \) K respectively. The magnetic part of the electrical resistivity of CeMg₃ exhibited a double peak structure and the magnetization measurement revealed a reduced magnetic moment of 0.5 \( \mu_B/\text{Ce} \). The heat capacity measurement of CeMg₃ measured down to 0.5 K exhibited an enlarged Sommerfeld coefficient of 370 mJ/K² mol. From the Schottky heat capacity we have estimated the crystal electric field split energy levels of CeMg₃ and NdMg₃.

1. Introduction
The magnetism due to the localized 4\( f \) electrons in the rare-earth based intermetallic systems is always interesting due to the wide range of physical properties exhibited by these compounds. The binary rare-earth intermetallic systems have been studied over several decades. In particular, the Ce based binary compounds are the most extensively studied as they exhibit many novel magnetic behavior owing to the close proximity of the 4\( f \) level to the Fermi level. In this paper we report on the magnetic properties of a simple binary system, RMg₃ (R = La, Ce, and Nd), which crystallize in the cubic BiF₃-type structure. In one of the early reports on RMg₃ system, Buschow has studied the magnetic properties of CeMg₃ and NdMg₃ and reported no magnetic ordering down to 4.2 K in these two compounds [1]. However, Galera et al and Pierre et al have found that CeMg₃ orders antiferromagnetically at 3.4 K [2, 3], while NdMg₃ orders at 6 K [3]. From the previous neutron scattering experiments on polycrystalline sample [4, 5], it has been found that NdMg₃ undergoes an antiferromagnetic ordering at \( T_N = 6 \) K with the propagation vector \( \mathbf{k} = (0.5, 0.5, 0.5) \). In this paper we report on the magnetic properties of single crystalline RMg₃ (R = La, Ce, and Nd) by studying the magnetic susceptibility, electrical transport and heat capacity measurements.

2. Experiment
From the binary phase diagrams of R-Mg (R = La, Ce, and Nd) by Nayeb-hasehmi and Clark [6], it was found that these compounds melt congruently at temperature close to 800 °C. Hence these
compounds can be grown directly from the melt. Because of the high vapor pressure of Mg, the single crystals were grown by Bridgman method by sealing it in a Molybdenum crucible. The molybdenum crucible was then subsequently sealed in a quartz ampoule and loaded into a box type furnace. The furnace was then raised to 850°C, well above the melting point of these compounds and held at this temperature for 24 hours, then slowly cooled down to 780°C over a period of 3 days. Bulk shiny single crystals were obtained by gently tapping on the alumina crucible. The crystals were then subjected to powder X-ray diffraction to check the phase purity. The orientation of the crystals were done by back reflection Laue method. The dc magnetic susceptibility and the magnetization measurements were performed in the temperature range 1.8-300 K using a superconducting quantum interference device (SQUID) and vibrating sample magnetometer (VSM). The heat capacity measurements were done in a Quantum Design physical property measurement system (PPMS).

3. Results

3.1. X-ray diffraction

Small pieces of the single crystals were crushed into fine powder and subjected to powder x-ray diffraction, using a PANalytical x-ray diffractometer with Cu-Kα radiation, to check the phase purity and to estimate the lattice constant values. No traces of any secondary phases were seen in the x-ray diffractogram indicating the samples are phase pure. A Rietveld analysis was performed and the representative powder x-ray diffraction pattern of LaMg\(_3\) is shown in Fig. 1. A reasonably good fit of the experimental pattern confirms the space group \(Fm\overline{3}m\) (#225) and the estimated lattice constant was 7.468 Å for LaMg\(_3\), 7.422 Å for CeMg\(_3\), and 7.363 Å for NdMg\(_3\). The crystals were then oriented along the principal crystallographic direction namely [100], by means of Laue back reflection. The four fold symmetry in the Laue pattern confirmed the cubic structure of these

![Figure 1. A representative powder X-ray diffraction pattern of fine powders of LaMg\(_3\) single crystal. The solid line through the experimental plots is the Rietveld refinement. The Bragg positions and the difference between the calculated and observed pattern is also shown.](image)
Figure 2. (a) Temperature dependence of magnetic susceptibility of CeMg$_3$ and NdMg$_3$ for field parallel to $H \parallel [100]$. The inset shows the low temperature part of the magnetic susceptibility. (b) Inverse magnetic susceptibility of CeMg$_3$ and NdMg$_3$, the solid lines are fit to Curie-Weiss law.

temperature, while NdMg$_3$ shows two transitions at 6.8 K and 2.8 K. At respective temperatures the compounds order antiferromagnetically. The heat capacity measurement to be discussed later confirms the bulk magnetic ordering at these temperatures. Figure 2(b) shows the inverse magnetic susceptibility. At high temperature the inverse magnetic susceptibility is linear and follows Curie-Weiss law for temperature greater than 200 K. The solid line in Fig. 2(b) is a fit to the Curie-Weiss law. From the fitting, effective magnetic moment $\mu_{\text{eff}}$ and the paramagnetic Curie temperature $\theta_p$ were found to be 2.61 $\mu_B$/Ce and -19.8 K for CeMg$_3$; and 3.62 $\mu_B$/Ce and -39.7 K for NdMg$_3$ respectively. The estimated effective moment is close to the free ion values of Ce and Nd in their trivalent state. The negative sign of the $\theta_p$ and the linear increase in the magnetization at the lowest measured temperature indicates the antiferromagnetic nature of the magnetic ordering.

Figure 3. Isothermal magnetization of CeMg$_3$ and NdMg$_3$ for $H \parallel [100]$ at $T = 1.8$ K.

The field dependence of magnetization $M(H)$ at a constant temperature $T = 1.8$ K is shown in Fig. 3. The magnetization is almost linear up to a field of 12 T, thus confirming the antiferromagnetic ordering of the Ce and Nd moments. The magnetization does not show any signature of saturation up to a field of 12 T and attains a value of only 0.5 $\mu_B$/Ce and 0.7 $\mu_B$/Nd, which are much less than the free ion moment values of respective atoms. The reduced value of the moment in CeMg$_3$ is attributed to the Kondo effect.
3.3. Heat Capacity

The temperature dependence of the specific heat capacity of single crystalline LaMg$_3$, CeMg$_3$ and NdMg$_3$ are shown in Fig. 4. The heat capacity of LaMg$_3$ does not show any anomaly, and its temperature dependence is typical for a non-magnetic reference compound. The low temperature part of the heat capacity of CeMg$_3$ is shown in the top inset of Fig. 4, where a clear jump is seen at $T_N = 2.6$ K, confirming the bulk magnetic ordering in this compound. The bottom inset shows the low temperature part of NdMg$_3$ heat capacity, and we see NdMg$_3$ shows two bulk ordering at 6.8 K and 2.8 K. The magnitude of the Sommerfeld coefficient is obtained by fitting the expression $C/T = \gamma + \beta T^2$. The $\gamma$, for CeMg$_3$ the value thus obtained is 370 mJ/mol K$^2$, indicating the heavy fermion nature of CeMg$_3$. Also shown in Fig. 4 is the Schottky heat capacity. From the analysis of Schottky heat capacity, we have estimated the crystal electric field splitting of the 5 fold and 10 fold degenerate levels of CeMg$_3$ and NdMg$_3$. The ground state of CeMg$_3$ is a doublet with an excited quartet state while for NdMg$_3$ the ground state is again a doublet with two excited quartet states. The corresponding energy level schemes are shown in the figure. We did not attempt to estimate the $\gamma$ value for NdMg$_3$ as the measurement was done only down to 2 K.

![Figure 4](image-url)

**Figure 4.** Temperature dependence of the specific heat capacity in LaMg$_3$, CeMg$_3$ and NdMg$_3$. Insets show the low temperature parts. The right panels show the Schottky heat capacity and the estimated energy levels. The ‘q’ and ‘d’ in the Schottky heat capacity of NdMg$_3$ represent the quartet and doublet levels respectively.

4. Conclusion

We have successfully grown the single crystal and studied the magnetic properties of RMg$_3$ (R = La, Ce and Nd). From the magnetic measurements it is evident that CeMg$_3$ orders antiferromagnetically at 2.6 K with a reduced moment and large Sommerfeld coefficient $\gamma$ thus indicating that CeMg$_3$ is a heavy fermion compound. On the otherhand, NdMg$_3$ exhibit two antiferromagnetic ordering at $T_{N1} = 6.8$ K and $T_{N2} = 2.8$ K which is confirmed by magnetic susceptibility, magnetization and heat capacity measurements.

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