Neutron diffraction studies on an exotic magnetic system, Nd$_7$Rh$_3$

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Abstract. Binary intermetallic compound Nd$_7$Rh$_3$ crystallizes in a Th$_7$Fe$_3$ type hexagonal structure in space group $P6_3mc$ and has been reported to show two antiferromagnetic (AFM) phase transitions at 32 K and 10 K from magnetic susceptibility, and a field induced first-order magnetic transition at a field strength of 1 Tesla at 2 K from magnetization measurements. These magnetic properties are different from the isostructural counterparts like Tb$_7$Rh$_3$, Ho$_7$Rh$_3$, and Nd$_7$Ni$_3$. In order to understand the differences in the magnetic behaviour between Nd$_7$Rh$_3$ and other isostructural compounds, we have carried out neutron diffraction (ND) studies on polycrystalline Nd$_7$Rh$_3$, at various temperatures between 2 and 45 K. ND patterns were also recorded at $T = 2K$ in the presence of applied magnetic fields from 0 to 1.5 Tesla. ND spectra on Nd$_7$Ni$_3$ and Ho$_7$Rh$_3$, for example, at 2 K in zero magnetic field exhibit a strong AFM peak at a $q$ (= $4\pi\sin(\theta)/\lambda$) value of 0.32 and 0.38 Å$^{-1}$, respectively. However, ND spectra on Nd$_7$Rh$_3$, carried out at Focusing Crystal Diffractometer (FCD-Dhruva-Mumbai), diffractometers E6 and E9 (HZB-Berlin) using wavelengths $\lambda = 1.48\text{Å}, 2.45\text{Å}$ and $2.8\text{Å}$ respectively, at $T = 2K$ in zero field do not exhibit any AFM peaks in the entire Q-range studied. Instead, long-range ferromagnetic order is established as evidenced by the intensity enhancement of the nuclear Bragg peaks. The lack of extra peaks in the ND patterns would imply that the magnetic order seen in magnetization could be of a $k = 0$ type which changes from one type to another on the application of magnetic field. The results of nuclear and magnetic structure refinement are discussed to explain the magnetic behaviour of Nd$_7$Rh$_3$ at low temperatures.

1. Introduction

The compound Nd$_7$Rh$_3$, crystallizes in Th$_7$Fe$_3$ type hexagonal structure in the space group $P6_3mc$ [1-2]. In this structure, Nd occupies three non-equivalent sites, 6c, 12d and 2b sites, whereas Rh occupies the 12d site, respectively. Magnetization studies on Nd$_7$Rh$_3$ exhibit two magnetic phase transitions, one at 32 K and the other at 10 K. At 32 K, Nd$_7$Rh$_3$ undergoes a transition from paramagnetic to an antiferromagnetic phase and that below 10 K; it undergoes another antiferromagnetic to ferromagnetic transition [2]. In addition to anomalous magnetic behavior, it has been reported by Tsutaoka et al [2] that Nd$_7$Rh$_3$ exhibits drastic changes in thermoelectric power below 50 K owing to changes in the
electronic structure, which might influence the magnetic structure at low temperatures. Nd$_7$Rh$_3$ exhibits a field-induced first-order magnetic phase transition at 1.8 K [3]. On the basis of isothermal magnetization and magnetoresistance measurements, it was shown that Nd$_7$Rh$_3$ exhibits magnetic phase co-existence phenomenon in the super-cooled state following this transition [3]. The anomalous transition at 10 K was also probed in detail using magnetic susceptibility, specific heat and magnetoresistance measurements, and it was observed that this transition is first-order like [4]. Recent studies on single-crystal of Nd$_7$Rh$_3$ have also conclusively established the anomalous magnetic behavior of Nd$_7$Rh$_3$ [5]. All these detailed studies revealed Nd$_7$Rh$_3$ is an interesting magnetic material which makes it different from isostructural compounds such as Ho$_7$Rh$_3$, Tb$_7$Rh$_3$, and Nd$_7$Ni$_3$, etc. Therefore, it is expected that the magnetic structure at low temperatures, for Nd$_7$Rh$_3$ will also be different from its isostructural counterparts. This is the primary motivation of this investigation.

2. Experimental Details

The intermetallic Nd$_7$Rh$_3$ was prepared in polycrystalline form by repeated arc-melting of stoichiometric ratio of Nd and Rh. The ingot thus obtained was annealed in a sealed quartz ampoule for over a few weeks to ensure homogeneity of the sample. The phase formation was checked by powder X-ray diffraction as well as by powder neutron diffraction at room temperature.

Initial characterization of the sample was done by measuring magnetization as a function of temperature and magnetic field using a commercial vibrating sample magnetometer. Powder neutron diffraction studies were carried out at room temperature at FCD (Dhruva, India) and at low temperatures on diffractometers E6 and E9 at BENS (HZB, Germany). The neutron diffraction (ND) data has been refined by Rietveld analysis method using the FULLPROF software package.

To overcome the problem of preferred orientation during ND measurements under applied magnetic field, the powder sample of Nd$_7$Rh$_3$ was mixed with a 1:1 solution of deuterated methanol and deuterated ethanol. Such a mixture helps in holding the grains of the polycrystalline sample intact under the application of magnetic field. The signal from this organic mixture is very minimal and is observed as a hump in the background. The sample and the mixture were contained in an aluminum can and loaded onto a liquid helium cryo-magnet for low temperature and in-field ND experiments.

3. Results and Discussions

3.1. Magnetization

In figure 1, magnetization data measured on the sample used for neutron diffraction has been shown. The two magnetic transitions expected at 32 and 10K and the irreversibility of the M(H) curve is clearly seen in the figure 1. The ZFC-FC bifurcation is also clearly seen in the inset figure. The observed behavior of M(H) and dc $\chi(T)$ are qualitatively same as reported in Refs. 3 and 4. It must be noted here that the magnetization measurements were carried out on a chunk of a polycrystalline sample.

3.2. Neutron Diffraction

3.2.1. Room temperature neutron diffraction: Neutron diffraction measurements at room temperature were carried out with a view to refine the crystal structure in the paramagnetic state of Nd$_7$Rh$_3$. The experiment was carried out in air on the Focussing crystal diffractometer (FCD) at Dhruva reactor at a wavelength of 1.48 Å. The Rietveld refined ND pattern is shown in figure 2. The refined structural parameters are listed in Table 1.
Figure 1 Magnetization (M) for Nd₇Rh₃ at T = 1.8 K is plotted against the ramping field (H). The black, green and blue arrows are indicative of the up down and up cycle of ramping field. The magnetic susceptibility measured in a field of 100 Oe is shown as an inset. The data has been measured in zero field cooled (ZFC) and field cooled (FC) state of the samples.

Table 1 Refined structural parameters of Nd₇Rh₃ at 300 K.

| Atom | Site | Symmetry | x    | y   | z    | B (Å²) |
|------|------|----------|------|-----|------|--------|
| Nd1  | 6c   | .m.      | 0.5394 | 0.4605 | 0.0075 | 0.0114 |
| Nd2  | 12d  | 1        | 0.8774 | 0.1259 | 0.3060 | 0.0100 |
| Nd3  | 2b   | 3m.      | 1/3   | 2/3  | 0.0220 | 0.0124 |
| Rh   | 12d  | 1        | 0.1773 | 0.7998 | 0.2535 | 0.0127 |

Figure 2 Rietveld refinement of the ND data of Nd₇Rh₃.
3.2.2 Low temperature neutron diffraction: ND studies on isostructural compounds such as Nd,Ni$_7$, [2, 6], Ho,Rh$_7$ [7] exhibit a strong magnetic peak around Q = 0.32 – 0.38 Å$^{-1}$. Q is the reciprocal space scattering vector, and is defined by $4\pi\sin\theta/\lambda$. If the magnetic structure of Nd,Rh$_7$ is similar to that of Nd,Ni$_7$ or Ho,Rh$_7$, etc, it could also exhibit a similar strong magnetic peak around similar Q values. Therefore, we carried out further ND experiments on Nd,Rh$_7$ at various temperatures between 2 and 45 K, and the patterns are shown in figure 3. The figure also shows the Rietveld refinement of T = 2 K data. The first and most significant difference in the ND pattern of Nd,Rh$_7$ and its isostructural compounds is the absence of the strong magnetic peak at lower angles (in terms of Q also there is no anomaly observed in the entire Q-range studied). ND data measured on both E6 and E9 diffractometers at T = 2K, is shown as a function of Q in the inset of figure 3. In the entire Q-range, no trace of the strong magnetic peak is found at lower angles.

Xu et al could refine the magnetic structure of Nd,Ni$_7$, assuming a helical magnetic structure and using propagation vector, $k = (0, 0, 1/3)$ [6]. Owing to the difference in the magnetic behaviour when compared to Nd,Ni$_7$ or Ho,Rh$_7$, it can be proposed that the magnetic structure of Nd,Rh$_7$ might be different from the one reported for Nd,Ni$_7$. Since there are no additional peaks attributable to magnetic ordering alone, the magnetic structure could be assumed to be having similar dimensions as that of the crystal structure and a propagation vector, $k = (0 0 0)$. All possible orientations for the three Nd sites were tried and it was found that the magnetic lines in the ND pattern of Nd,Rh$_7$ could be fitted fairly well assuming a collinear magnetic ordering along $c$-axis. With increasing temperature there is a slight decrease in the intensity of some nuclear peaks, affecting the magnetic moment on three non-equivalent Nd sites. No moment was observed on Rh even at lowest temperature. The magnetic moment on Nd calculated from the refinement is listed in Table 2.

In order to ascertain the effect of magnetic field on the magnetic structure, we have also measured ND patterns at T = 2 K under various applied fields. In figure 4, the ND patterns recorded at H = 0, 1.5 and 5 Tesla are shown. The refined ND pattern for H = 0 is shown again for direct comparison. As can be clearly seen from the ND patterns, the effect of magnetic field is very minimal on the diffraction peaks, even for a strong field of 5 Tesla. The magnetic moment on Nd obtained from the Rietveld analysis of all the in-field diffraction patterns is also recorded in the Table 2. It is seen that the moments at the three Nd sites respond in an unequal manner along $c$-axis while in reality, it is
likely that the magnetic ordering in this compound is quite complex whose net effect is to suppress any strong long-range antiferromagnetic interactions.

The moments on Nd sites are plotted as a function of temperature of measurement in figure 5. The moment values increase with decreasing temperature and reach maxima at around 15 K and fall below 10 K, thus signifying the changes in the magnetic structure corresponding to the anomalies observed in magnetic measurements. The values of magnetic moment on Nd atom observed at T = 2K from ND experiments are close to the saturation magnetization values observed at T = 1.8K. We see a finite moment even at 45 K, which can imply the existence of short range magnetic correlations well above 30 K.

### Table 2
Magnetic moments (M) on Nd atom obtained from the Rietveld analysis of ND data at various temperatures and also at various fields at T = 2K.

| M(µB) | T          |
|-------|------------|
|       | 2 K        | 7.5 K | 15 K | 25 K | 35 K | 45 K |
|       | H  = 0     | 1.5 T | 5 T  |
| µNd1  | 1.938      | 2.064 | 0.599| 2.297| 2.878| 2.171| 1.930| 0.886|
| µNd2  | 2.426      | 1.886 | 3.273| 2.418| 2.725| 1.428| 2.195| 1.102|
| µNd3  | 1.675      | 1.203 | 1.212| 1.270| 2.128| 1.718| 1.888| 0.612|

Figure 4 ND patterns recorded at T = 2K under fields of 0, 1.5 and 5 T on E6. The Rietveld refinement of H = 0T data is also shown in the figure.

### 4. Conclusions

Neutron diffraction experiments were carried out on polycrystalline sample of Nd.Rh to determine the magnetic structure at low temperatures. A magnetic structure with unequal magnetic
moments on three non-equivalent Nd sites has been observed. ND studies show that Nd,Rh₃ exhibits a kind of magnetic structure which changes from one type to another in the presence of magnetic field, as observed by the changes in the magnetic moments on Nd. Another observation that makes Nd,Rh₃ an interesting compound is that the diffraction patterns look similar before and after the first order transition. Naturally, the magnetization of this compound is quite different from its isostructural Nd,Ni₃. More detailed studies are required to understand the exact nature of magnetic structure and neutron diffraction experiments on single crystal of Nd,Rh₃ can give more insight on the magnetic structure and order of this magnetically exotic compound.

![Graph](image)

**Figure 5** The variation of the magnetic moments on three non-equivalent Nd sites is plotted against the temperatures at which ND patterns were recorded. The moments were obtained from the Rietveld analysis.

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