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Magnetic and neutron diffraction studies of the ordered perovskite Ba_2NdRuO_6†

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The magnetic properties of the ordered perovskite compound Ba_2NdRuO_6 are reported. Powder neutron diffraction measurements were performed at 100, 35 and 7 K to determine its crystal structure and magnetic properties. Refinement of the data collected at 100 K showed that this compound has monoclinic symmetry, space group $P2_1/n$ with $a = 5.9888(2)$, $b = 5.9916(2)$, $c = 8.4667(2)$ Å and $\beta = 90.026(3)°$, and that the structure is that of a perovskite with a 1 : 1 ordered arrangement of Ru^{5+} and Nd^{3+} over the 6-coordinate sites. From the data collected at 35 and 7 K, it was found that there is a long range antiferromagnetic ordering in the Ba_2NdRuO_6. The magnetic structure is of type I and the magnetic moments of Nd^{3+} and Ru^{5+} ions are in the same direction in the *ab* plane.

1 Introduction

Ordered perovskite-type oxides, A_2LnMO_6 (A = alkaline-earth element; Ln = lanthanide element; M = 4d or 5d transition element), in which the Ln and M elements are regularly ordered show a variety of magnetic behaviors at low temperature. We are particularly interested in such compounds containing pentavalent ruthenium ions. The electronic structure of Ru^{5+} is $[Kr]4d^3$ ([Kr]: krypton core). Such highly oxidized cations from the second transition series sometimes show quite unusual magnetic behavior. When the Ln ion is diamagnetic (*e.g.* Y^{3+}, La^{3+} and Lu^{3+}), such A_2LnRuO_6 compounds are suitable for studying the behavior of Ru^{5+} ions, since only the Ru^{5+} ions are responsible for their magnetic properties.[1,2] Battle *et al.* investigated the crystal structures and magnetic properties of Ba_2LnRuO_6 (Ln = Y, La and Lu), and reported that these compounds show antiferromagnetic transitions at *ca.* 15–30 K. The crystal structures of Ba_2YRuO_6 and Ba_2LuRuO_6 are both cubic at room temperature, space group $Fm3m$, and they exhibit Type I antiferromagnetism at low temperature.[3] They also demonstrated that the crystal structure of Ba_2LaRuO_6 adopts triclinic symmetry at room temperature, space group $P\bar{1}$, and that the magnetic structure at 2 K is a Type III antiferromagnetic arrangement.[4]

We have turned our attention to the crystal structures and magnetic properties of the ordered perovskites A_2NdRuO_6, in which both Nd^{3+} and Ru^{5+} ions are responsible for its magnetic behavior. It was reported that the Nd cation in the Ca_2NdRuO_6 occupies only the A site of the ABO_3 perovskite and that the Nd^{3+} and Ca^{2+} ions are disordered on the A site, *i.e.* the formulation $CaNd[CaRu]O_6$ is more appropriate for this compound.[5] Doi and Hinatsu reported that, although they tried to prepare Sr_2NdRuO_6, its preparation was unsuccessful due to the large size of the Nd^{3+} ion compared with that of Sr^{2+}, and that even a compound in which the Nd cation occupies the A site of the perovskite was not prepared.[6] In this study, we have successfully prepared Ba_2NdRuO_6, which is the only obtainable ordered perovskite-type compound in the A_2NdRuO_6 family. Through magnetic susceptibility, heat capacity and neutron diffraction measurements, it has been found that this compound shows an antiferromagnetic transition at *ca.* 58 K. Herein, we will report these experimental results and discuss the magnetic properties of Ba_2NdRuO_6.

2 Experimental

A polycrystalline sample of Ba_2NdRuO_6 was synthesized by heating stoichiometric amounts of $BaCO_3$, Nd_2O_3 and RuO_2, first at 900 °C for 12 h and then 1300 °C for 60 h, in air with frequent grinding. X-Ray diffraction measurements were performed with Cu-Kα radiation on a Rigaku RINT 2100 diffractometer equipped with a curved graphite monochromator.

Powder neutron diffraction measurements were performed at 100, 35 and 7 K using the high resolution powder diffractometer (HRPD) at the JRR-3M reactor (Japan Atomic Energy Research Institute), with a Ge(331) monochromator ($\lambda = 1.8230$ Å). The collimators used were 6′-20′-6′ and were placed before and after the monochromator, and between the sample and each detector. The set of 64 detectors and collimators, which were placed every 2.5°, rotate around the sample. Crystal and magnetic structures were determined by the Rietveld technique, using the RIETAN program.[7]

The temperature dependence of the magnetic susceptibility was measured in the temperature range 2–300 K in a magnetic field of 0.1 T with a SQUID magnetometer (Quantum Design, Model MPMS); the susceptibility data were collected both after cooling the sample from room temperature to 2 K in zero-field (ZFC) and after cooling in an applied field of 0.1 T (FC).

The heat capacity measurements were carried out using a relaxation technique supplied by a commercial heat capacity measurement system (Quantum Design, Model PPMS) in the temperature range from 2 to 300 K. The sample, in the form of a pellet (*ca.* 10 mg), was mounted on an aluminium plate with Apiezon grease for better thermal contact.

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†Electronic supplementary information (ESI) available: powder XRD profiles, crystal structure and powder neutron diffraction profiles [at 100 (a), 35 (b) and 7 K (c)] for Ba_2NdRuO_6. See http://www.rsc.org/suppdata/jm/b0/b003629n/

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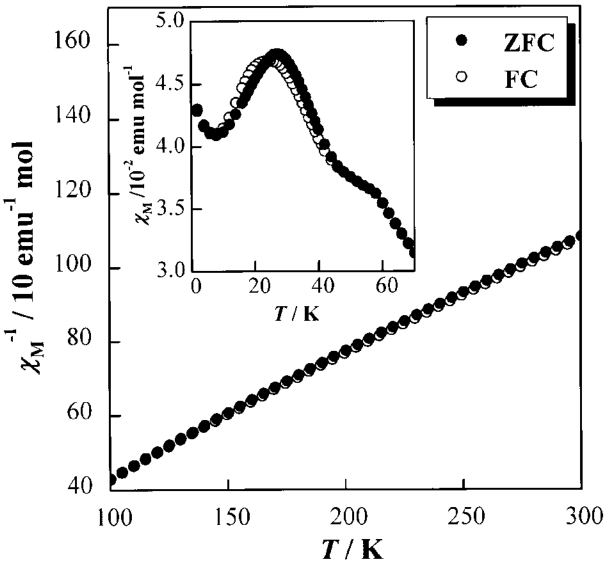

Fig. 1 Temperature dependence of the ZFC (filled symbols) and FC (open symbols) molar magnetic susceptibilities for Ba_2NdRuO_6 in an applied field of 0.1 T.

3 Results and discussion

3.1 Crystal structure

The results of the powder X-ray diffraction measurements show that Ba_2NdRuO_6 was formed as a single phase with a perovskite-type structure. The X-ray diffraction pattern is available as ESI.† The pattern was indexed on a monoclinic unit cell, in space group $P2_1/n$, which permits an ordered arrangement of Nd^{3+} and Ru^{5+} ions over the B-sites of the ABO_3 perovskite. The structural analysis using the Rietveld method, which was carried out with the RIETAN program,[7] shows that the Nd^{3+} and Ru^{5+} ions are arranged alternately and that they have a rock salt sublattice. The approximate size of the unit cell is $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$, where a_p is a lattice parameter in a primitive cubic unit cell. The observed and calculated X-ray diffraction profiles, and the differences between them are available as ESI.† The reliability factors are as follows: $R_{wp} = 12.07$, $R_I = 1.44$ and $R_F = 3.70\%$. The diffraction profile shows the existence of superlattice reflections [ex. (011) and (101)] which come from the ordered array between the Nd and Ru cations. The Nd and Ru cations are therefore arranged regularly over the octahedral (B) sites and form two interpenetrating face-centered sublattices. The crystal structure of Ba_2NdRuO_6 is shown in the ESI.† The lattice parameters are $a = 5.9888(2)$, $b = 5.9916(2)$, $c = 8.4667(2)$ Å and $\beta = 90.026(3)°$. Since the angle of β is nearly 90°, the monoclinic distortion of this compound is very small.

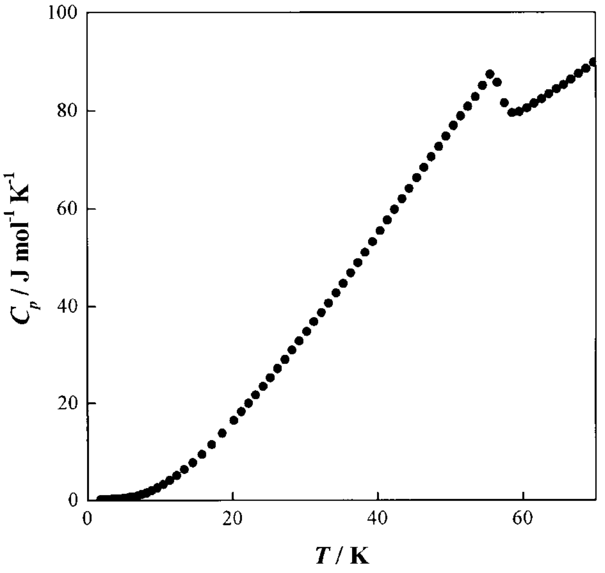

Fig. 2 Temperature dependence of the heat capacity of Ba_2NdRuO_6.

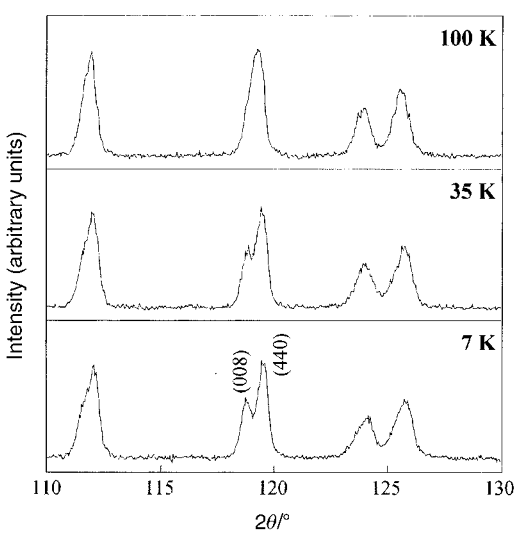

Fig. 3 Enlarged neutron diffraction profiles around $2\theta \approx 120°$ at each temperature.

3.2 Magnetic properties

3.2.1 Magnetic susceptibility. The temperature dependence of the molar magnetic susceptibilities for Ba_2NdRuO_6 is shown in Fig. 1. There is a slight divergence between the ZFC and FC susceptibilities. Two magnetic anomalies have been found in the susceptibility *vs.* temperature curve, *i.e.* a maximum in the susceptibility appears at *ca.* 27 K and an inflection occurs at *ca.* 58 K.

Table 1 Structural parameters for Ba_2NdRuO_6 (space group $P2_1/n$)[a]

Atom	Site	x	y	z	B/Å^2	μ/μ_B
At 100 K						
Ba	4e	−0.001(3)	−0.003(8)	0.249(3)	0.06(7)	
Nd	2d	1/2	0	0	0.09(4)	
Ru	2c	1/2	0	1/2	0.09(4)	
O(1)	4e	0.227(4)	0.267(4)	0.015(6)	0.42(5)	
O(2)	4e	0.234(4)	−0.276(3)	−0.014(6)	0.42(5)	
O(3)	4e	−0.032(2)	0.503(9)	0.232(2)	0.42(5)	
$a = 5.9920(2)$, $b = 5.9765(2)$, $c = 8.4480(3)$ Å, $\beta = 90.02(1)°$, $V = 302.53(2)$ Å^3, $R_{wp} = 8.24$, $R_I = 1.62$, $R_F = 1.53$, $R_e = 6.15\%$						
At 35 K						
Ba	4e	0.016(1)	0.001(3)	0.250(1)	0.61	
Nd	2d	1/2	0	0	0.29	1.9(1)
Ru	2c	1/2	0	1/2	0.020	1.8(1)
O(1)	4e	0.216(6)	0.243(3)	0.010(2)	0.77	
O(2)	4e	0.214(6)	−0.251(3)	0.007(2)	0.62	
O(3)	4e	−0.026(2)	0.492(2)	0.231(1)	0.40	
$a = 5.9734(3)$, $b = 5.9722(3)$, $c = 8.4737(3)$ Å, $\beta = 90.183(3)°$, $V = 302.29$ Å^3, $R_{wp} = 9.83$, $R_I = 2.18$, $R_F = 1.47$, $R_e = 6.41\%$						
At 7 K						
Ba	4e	0.019(1)	0.001(2)	0.246(1)	0.061	
Nd	2d	1/2	0	0	0.29	2.3(1)
Ru	2c	1/2	0	1/2	0.061	2.2(1)
O(1)	4e	0.215(6)	0.250(4)	0.007(3)	0.77	
O(2)	4e	0.216(5)	−0.251(3)	0.007(3)	0.8(2)	
O(3)	4e	−0.027(2)	0.486(2)	0.232(1)	0.4(2)	
$a = 5.9715(3)$, $b = 5.9709(3)$, $c = 8.4761(3)$ Å, $\beta = 90.178(3)°$, $V = 302.22$ Å^3, $R_{wp} = 10.88$, $R_I = 2.93$, $R_F = 1.80$, $R_e = 6.42\%$						

[a] The reliability factors R_{wp}, R_I, R_F and R_e are defined as follows: $R_{wp} = [\sum w(|F(o)| - |F(c)|)^2 / \sum w|F(o)|^2]^{1/2}$, $R_I = \sum |I_k(o) - I_k(c)| / \sum I_k(o)$, $R_F = \sum \left| [I_k(o)]^{1/2} - [I_k(c)]^{1/2} \right| / \sum [I_k(o)]^{1/2}$ and $R_e = \left(\frac{N-p}{\sum w|F(o)|^2} \right)^{1/2}$.

Table 2 Bond lengths (Å) and angles (°) for Ba_2NdRuO_6

At 100 K					
Nd–O(1)	2.29(3) × 2		Ru–O(1)	1.95(3) × 2	
Nd–O(2)	2.30(3) × 2		Ru–O(2)	1.94(3) × 2	
Nd–O(3)	2.27(1) × 2		Ru–O(3)	1.97(1) × 2	
O(1)–Nd–O(2)	90.0(6)	O(1)–Ru–O(2)	90.8(7)	Nd–O(1)–Ru	173.1
O(1)–Nd–O(3)	90.0(14)	O(1)–Ru–O(3)	90.6(20)	Nd–O(2)–Ru	173.3
O(2)–Nd–O(3)	90.7(14)	O(2)–Ru–O(3)	90.2(20)	Nd–O(3)–Ru	169.6
At 35 K					
Nd–O(1)	2.23(3) × 2		Ru–O(1)	2.01(3) × 2	
Nd–O(2)	2.28(3) × 2		Ru–O(2)	1.96(3) × 2	
Nd–O(3)	2.28(1) × 2		Ru–O(3)	1.97(1) × 2	
O(1)–Nd–O(2)	98.2(6)	O(1)–Ru–O(2)	99.1(7)	Nd–O(1)–Ru	169.5
O(1)–Nd–O(3)	91.4(14)	O(1)–Ru–O(3)	90.5(20)	Nd–O(2)–Ru	171.3
O(2)–Nd–O(3)	90.6(14)	O(2)–Ru–O(3)	92.4(20)	Nd–O(3)–Ru	171.1
At 7 K					
Nd–O(1)	2.24(3) × 2		Ru–O(1)	2.00(3) × 2	
Nd–O(2)	2.26(3) × 2		Ru–O(2)	1.97(3) × 2	
Nd–O(3)	2.28(1) × 2		Ru–O(3)	1.98(1) × 2	
O(1)–Nd–O(2)	97.9(6)	O(1)–Ru–O(2)	98.8(7)	Nd–O(1)–Ru	169.8
O(1)–Nd–O(3)	92.1(14)	O(1)–Ru–O(3)	91.2(20)	Nd–O(2)–Ru	171.5
O(2)–Nd–O(3)	90.0(14)	O(2)–Ru–O(3)	93.2(20)	Nd–O(3)–Ru	170.1

Fitting the Curie–Weiss law to the temperature dependence of the magnetic susceptibilities in the temperature range 100 to 300 K gives an effective magnetic moment ($\mu_{\rm eff}$) of $4.96\mu_B$ and a Weiss constant (θ) of −35.5 K. The predominant magnetic interaction in this compound seems to be antiferromagnetic, judging from this negative Weiss constant. This $\mu_{\rm eff}$ value is in reasonable agreement with the value of 5.12 μ_B reported previously for Ca_2NdRuO_6.[4] Since the theoretical moment of the Nd^{3+} ion is 3.62 μ_B, the magnetic moment for the Ru^{5+} ion in Ba_2NdRuO_6 is estimated to be 3.39 μ_B from the relation $\mu_{\rm eff}(Ba_2NdRuO_6)^2 = \mu_{\rm eff}(Nd^{3+})^2 + \mu_{\rm eff}(Ru^{5+})^2$. Comparable magnetic moment values have been obtained for Ba_2BRuO_6 (B = Y, La, Lu: diamagnetic)[4,8] and Sr_2BRuO_6 (B = Y, Lu).[2,8]

3.2.2 Heat capacity. Fig. 2 shows the temperature dependence of the heat capacity for Ba_2NdRuO_6. A λ-type anomaly can be seen at 58 K, which corresponds to the antiferromagnetic transition observed in the magnetic susceptibility *vs.* temperature curve. No anomaly corresponding to the maximum observed at *ca.* 27 K in the susceptibility *vs.* temperature curve was detected in the heat capacity measurements.

3.2.3 Neutron diffraction. *(a) Crystal structure.* X-Ray diffraction data collected at room temperature indicate that Ba_2NdRuO_6 has monoclinic symmetry. Powder neutron diffraction profiles for Ba_2NdRuO_6 measured at 100, 35 and 7 K are available as ESI.† Refinements of the crystal structure with the neutron diffraction data measured at 100, 35 and 7 K were carried out by the Rietveld analysis technique. Fig. 3 shows enlarged neutron diffraction profiles around $2\theta \approx 120°$ at each temperature. At 100 K, the reflection due to the (008) and (440) planes is observed as a single peak, while at 7 and 35 K, it is separated into two peaks. These experimental results are due to the fact that the monoclinic distortion is less prominent at 100 K, and increases with decreasing temperature. Atomic positions and lattice parameters at 100, 35 and 7 K are tabulated in Table 1. At 100 K, this compound has lattice parameters of $a = 5.9920(2)$, $b = 5.9765(2)$, $c = 8.4480(3)$ Å and $\beta = 90.02(1)°$. With decreasing temperature, the lattice shrinks in the direction of the *a* axis, but stretches in the direction of the *c* axis and the angle β increases from 90°. Selected bond lengths and angles for Ba_2NdRuO_6 at 100, 35 and 7 K are tabulated in Table 2. At 100 K, the O–Nd–O bond angles are approximately equal and nearly 90°. The same is true for the O–Ru–O bond angles, that is to say, both the Nd^{3+} ion and the Ru^{5+} ion are in an almost octahedral environment, surrounded by six oxygen ions. At lower temperatures (35 and 7 K), the O–Nd–O (and O–Ru–O) bond angles are no longer equal, and depart considerably from 90°, which means that the oxygen coordination around the Nd^{3+} (and Ru^{5+}) ions is not octahedral. The three Nd–O–Ru bond angles are approximately equal.

(b) Magnetic structure. Since the magnetic anomaly was observed at 27 and 58 K in the susceptibility *vs.* temperature curve, we performed neutron diffraction measurements at 100, 35 and 7 K.

In the neutron diffraction profiles collected at 35 and 7 K

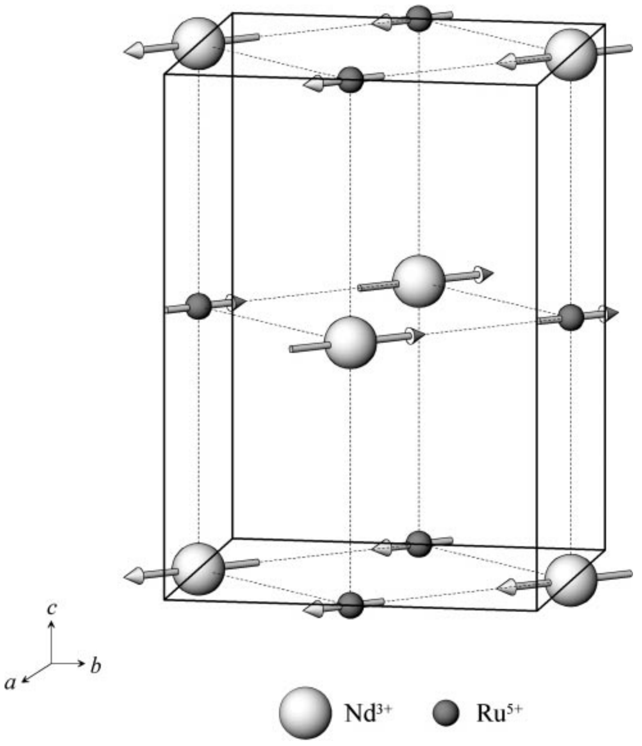

Fig. 4 The magnetic structure of Ba_2NdRuO_6. Diamagnetic ions are omitted. Larger circles Nd^{3+}; smaller circles Ru^{5+}. The direction of the magnetic moments in the *ab* plane was not determined in this experiment.

(see ESI†), a number of low-angle peaks for magnetic reflections which are not observed at 100 K appear, indicating that Ba_2NdRuO_6 shows the existence of antiferromagnetic ordering at these temperatures. We tried to determine the magnetic structure of Ba_2NdRuO_6 from the diffraction data collected at 7 K and 35 K using the analysis program RIETAN.[7] There is no difference between the profiles measured between at 35 K and at 7 K, except for a variation in the intensities of the magnetic peaks, which indicates that two kinds of magnetic ions (Nd^{3+} ion and Ru^{5+} ion) magnetically order at the same temperature, 58 K. This is consistent with the results of heat capacity measurements that a λ-type anomaly occurs at this temperature. The anomaly found at *ca.* 27 K in the susceptibility *vs.* temperature curve was not observed in the heat capacity measurements. The reason for this is not clear at present, but one possibility is that a reorientation of the magnetic moments may occur at this temperature.[9]

It has been reported that most of the magnetic structures of the antiferromagnets A_2BRuO_6 (A = Sr, Ba, B = Y, Lu) are Type I (for Ba_2LaRuO_6 it is Type III).[3,4] First of all, we carried out the determination of the magnetic structure of Ba_2NdRuO_6 by considering the magnetic structural data for Ba_2BRuO_6 (B = La, Y, Lu) and Sr_2BRuO_6 (B = Ho, Er). The large (001) magnetic peak ($2\theta \approx 12°$) is observed in the profiles of Ba_2NdRuO_6 at 35 and 7 K, but the (100) or (010) magnetic peak ($2\theta \approx 18°$) is not seen, indicating that the alignment of the magnetic moments is parallel not to the *c* axis, but to the *a* or *b* axes. Unfortunately, we could not definitely determine the direction of the magnetic moments from these powder neutron diffraction data. The magnetic structure determined for this compound is illustrated in Fig. 4, *i.e.* the magnetic type is Type I. Both Nd^{3+} and Ru^{5+} ions exist on the *ab* plane. The magnetic moments of both were found to be in the same direction from the analysis of the powder neutron diffraction measurements, therefore, the *ab* plane would seem to be a ferromagnetic plane. This result is in contrast to the cases for Sr_2HoRuO_6[10] and Sr_2ErRuO_6,[5] in which the directions of the magnetic moments of Ho^{3+} and Ru^{5+} ions in the *ab* plane are antiparallel with each other, *i.e.* they order ferrimagnetically. From the Rietveld analysis, the ordered magnetic moments at 35 K are determined to be 1.9(1) for Nd^{3+} and 1.8(1) μ_B for Ru^{5+}, and at 7 K they are 2.3(1) for Nd^{3+} and 2.2(1) μ_B for Ru^{5+}. This is the same tendency as the results for Sr_2ErRuO_6 and Sr_2HoRuO_6 reported previously, *i.e.* the more the temperature decreases, the more the ordered magnetic moments increase, but they do not saturate, even at 4.2 K.

In order to elucidate various kinds of magnetic structures, we are studying the magnetic properties of a series of Ba_2LnRuO_6 compounds through powder neutron diffraction measurements.

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