

Article

Charge- and Orbital-Order Transitions in the A-Site-Ordered Quadruple Perovskite $\text{NdCuMn}_6\text{O}_{12}$

Alexei A. Belik ^{1,*} , Ran Liu ^{1,2,3} , Lei Zhang ^{1,2}, Yoshitaka Matsushita ⁴  and Kazunari Yamaura ^{1,2} 

¹ Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba 305-0044, Ibaraki, Japan; liu.ran@sanken.osaka-u.ac.jp (R.L.); yamaura.kazunari@nims.go.jp (K.Y.)

² Graduate School of Chemical Sciences and Engineering, Hokkaido University, North 10 West 8, Kita-ku, Sapporo 060-0810, Hokkaido, Japan

³ Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Osaka 567-0047, Ibaraki, Japan

⁴ National Institute for Materials Science (NIMS), Sengen 1-2-1, Tsukuba 305-0047, Ibaraki, Japan; matsushita.yoshitaka@nims.go.jp

* Correspondence: alexei.belik@nims.go.jp

Abstract

$\text{AMn}_7\text{O}_{12}$ perovskites (with A = divalent elements) show complex structural and magnetic transitions including incommensurate orbital density waves and coupled/decoupled modulated spin helicity originating from charge-ordered $\text{Mn}^{3+}/\text{Mn}^{4+}$ cations with the 3:1 ratio at the B perovskite sites and unusual apically compressed Jahn–Teller distortions of MnO_6 octahedra. The same $\text{Mn}^{3+}:\text{Mn}^{4+}$ ratio can be achieved in $\text{RCuMn}_6\text{O}_{12}$ compositions, where R is a trivalent rare-earth cation. Therefore, the comparison in behavior of $\text{AMn}_7\text{O}_{12}$ and $\text{RCuMn}_6\text{O}_{12}$ is of interest. In this work, the A-site-ordered quadruple perovskite $\text{NdCuMn}_6\text{O}_{12}$ was prepared by a high-pressure high-temperature method. Its structural properties were investigated by synchrotron powder X-ray diffraction between 100 K and 350 K and laboratory powder X-ray diffraction between 5 K and 300 K. It shows a first-order structural phase transition from $Im\bar{3}$ symmetry (at high temperatures) to $R\bar{3}$ symmetry near 292 K. The structural transition is accompanied by charge ($\text{Mn}^{3+}/\text{Mn}^{4+}$) and unusual orbital (on the Jahn–Teller active Mn^{3+} cations located in MnO_6 octahedra) orders. However, no additional structural/orbital modulations were found at lower temperatures in comparison with $\text{AMn}_7\text{O}_{12}$. Magnetic properties were investigated by temperature- and field-dependent magnetization and specific heat measurements, where a ferrimagnetic transition was found near 120 K. In addition, low-temperature magnetic anomalies were observed near 20 K, probably originating from the Nd sublattice.

Keywords: A-site-ordered quadruple perovskites; orbital order; charge order; high-pressure synthesis



Academic Editor: Marius Andruh

Received: 21 May 2026

Revised: 18 June 2026

Accepted: 24 June 2026

Published: 26 June 2026

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1. Introduction

Manganites have played an important role in the science of perovskite-structure materials since the 1950s [1,2]. They were used for understanding the interplay between charge, spin, and orbital degrees of freedom and the crystal lattice in transition-metal oxides and developing such concepts as small polarons, double exchange, electron–phonon couplings, and Jahn–Teller (JT) distortions [3–5].

A lot of papers were published on simple perovskite $R_{1-x}A_x\text{MnO}_3$ manganites, where R is a rare-earth cation and A is a divalent cation [3–5], and detailed composition–temperature phase diagrams were constructed [3–6]. Charge-ordering (CO) phenomena were often observed at some special doping levels, such as near $x = 0.5$ (half-doped), $x = 1/3$ (one-third-doped), $x = 1/4$ (quarter-doped), and others. In addition to different CO patterns, orbital ordering (OO) on sites containing Mn^{3+} cations is realized, and complex spin orderings take place coupled with underlying charge-ordered and orbital-ordered structures.

A-site-ordered quadruple perovskites [7–11] with the general composition of $AA'_3\text{B}_4\text{O}_{12}$ form a different playground to manipulate charge, spin, and orbital degrees of freedom. Such manganites, $\text{AMn}_3\text{Mn}_4\text{O}_{12}$ or $\text{AMn}_7\text{O}_{12}$ in short [10,11], intrinsically have different ratios of Mn^{3+} and Mn^{4+} cations (at the perovskite B sites) without any doping, depending on the oxidation state of the A cation. With $A = \text{Na}^+$ [12,13], the $\text{Mn}^{4+}:\text{Mn}^{3+}$ ratio is 1:1 (half-doped). With $A = \text{Mn}^{2+}$, Ca^{2+} , Cd^{2+} , Sr^{2+} , Hg^{2+} , and Pb^{2+} [14–23], the $\text{Mn}^{4+}:\text{Mn}^{3+}$ ratio is 1:3 (quarter-doped). Among different $\text{AMn}_7\text{O}_{12}$ compounds, $\text{CaMn}_7\text{O}_{12}$ ($= [\text{Ca}^{2+}\text{Mn}_3^{3+}][\text{Mn}_3^{3+}\text{Mn}^{4+}]\text{O}_{12}$) was the most studied compound because it is the only composition that can be prepared at ambient pressure [15]. $\text{CaMn}_7\text{O}_{12}$ [10] shows a CO transition below $T_{\text{CO}} = 409\text{--}448\text{ K}$ (T_{CO} is a CO transition temperature) with the $Im\bar{3}$ symmetry above T_{CO} and $R\bar{3}$ symmetry below T_{CO} . The $R\bar{3}$ structure has apically compressed Mn^{3+}O_6 octahedra with four longer and two shorter Mn–O distances [16] while usual JT systems have two longer and four shorter Mn–O distances. $\text{CaMn}_7\text{O}_{12}$ shows another transition below $T_{\text{OO}} = 260\text{ K}$ with an incommensurate structural modulation and propagation vector, $k_s = (0, 0, \sim 0.92)$. The incommensurate structure has a complex modulation of Mn–O bond distances interpreted as an incommensurate orbital density wave localized on the B-site Mn^{3+} cations, and the majority of MnO_6 octahedra in this structure are locally elongated along one of two axes with certain periods resulting in the apparent apical compression of MnO_6 octahedra on average. $\text{CaMn}_7\text{O}_{12}$ shows the first long-range magnetic ordering transition below $T_{\text{N1}} = 90\text{ K}$ with an incommensurate propagation vector locked to the structural modulation [18]. Below the second magnetic transition at $T_{\text{N2}} = 48\text{ K}$, the magnetic structure delocks from the structural modulation giving rise to a complex multi- k magnetic ground state [18]. Magnetic structures of $\text{CaMn}_7\text{O}_{12}$ break the inversion symmetry producing spin-induced ferroelectric polarization [17,18]. The similar picture of complex structural and magnetic phase transitions is realized in other members of the $\text{AMn}_7\text{O}_{12}$ series with $A = \text{Mn}$, Cd , Sr , Hg , and Pb [10,20–23]. Therefore, $\text{AMn}_7\text{O}_{12}$ compounds and their variations, such as $\text{CaCu}_x\text{Mn}_{7-x}\text{O}_{12}$ solid solutions [24–37] with $0 \leq x \leq 3$, have attracted a lot of attention in the literature. For example, compounds with large Cu contents show robust ferrimagnetic properties above room temperature [31,37], large low-field magnetoresistance [32,33,36], and magnetocaloric properties [34]. $\text{AMn}_7\text{O}_{12}$ compounds and their variations show good catalytic properties [38].

The $\text{Mn}^{4+}:\text{Mn}^{3+}$ ratio of 1:3 at the B sites can also be achieved in the following compositions: $\text{RCuMn}_6\text{O}_{12}$ ($= [\text{R}^{3+}\text{Cu}^{2+}\text{Mn}_2^{3+}][\text{Mn}_3^{3+}\text{Mn}^{4+}]\text{O}_{12}$), where R is a trivalent rare-earth cation, which are the members of more general solid solutions with the composition of $\text{RCu}_x\text{Mn}_{7-x}\text{O}_{12}$ [39–54] and with $x = 1$. Therefore, it could be interesting to compare the structural and magnetic properties of the $\text{AMn}_7\text{O}_{12}$ and $\text{RCuMn}_6\text{O}_{12}$ series. In this work, we prepared one member of the $\text{RCuMn}_6\text{O}_{12}$ series with $\text{R} = \text{Nd}$ using a high-pressure high-temperature method. $\text{NdCuMn}_6\text{O}_{12}$ shows a CO transition near 290 K from $Im\bar{3}$ symmetry (above 290 K) to $R\bar{3}$ symmetry (below 290 K). The $R\bar{3}$ symmetry remains down at 5 K without any additional structural distortions/modulations in comparison with the $\text{AMn}_7\text{O}_{12}$ series. $\text{NdCuMn}_6\text{O}_{12}$ also shows a ferrimagnetic transition below 120 K and a second magnetic transition near 20 K probably originating from the Nd sublattice, again in comparison with the $\text{AMn}_7\text{O}_{12}$ series.

2. Results and Discussion

No impurity reflections were detected even on high-resolution, high-intensity synchrotron powder X-ray diffraction (XRD) data of the prepared $\text{NdCuMn}_6\text{O}_{12}$ samples confirming the high quality of the samples. However, room-temperature (RT) XRD data (laboratory and synchrotron) showed the presence of two phases, cubic $Im\bar{3}$ and trigonal $R\bar{3}$, because a structural phase transition temperature is very close to RT (292 K, see below). Therefore, we show synchrotron XRD patterns at 100 K and 350 K (not at RT) in Figure 1 to demonstrate the sample quality.

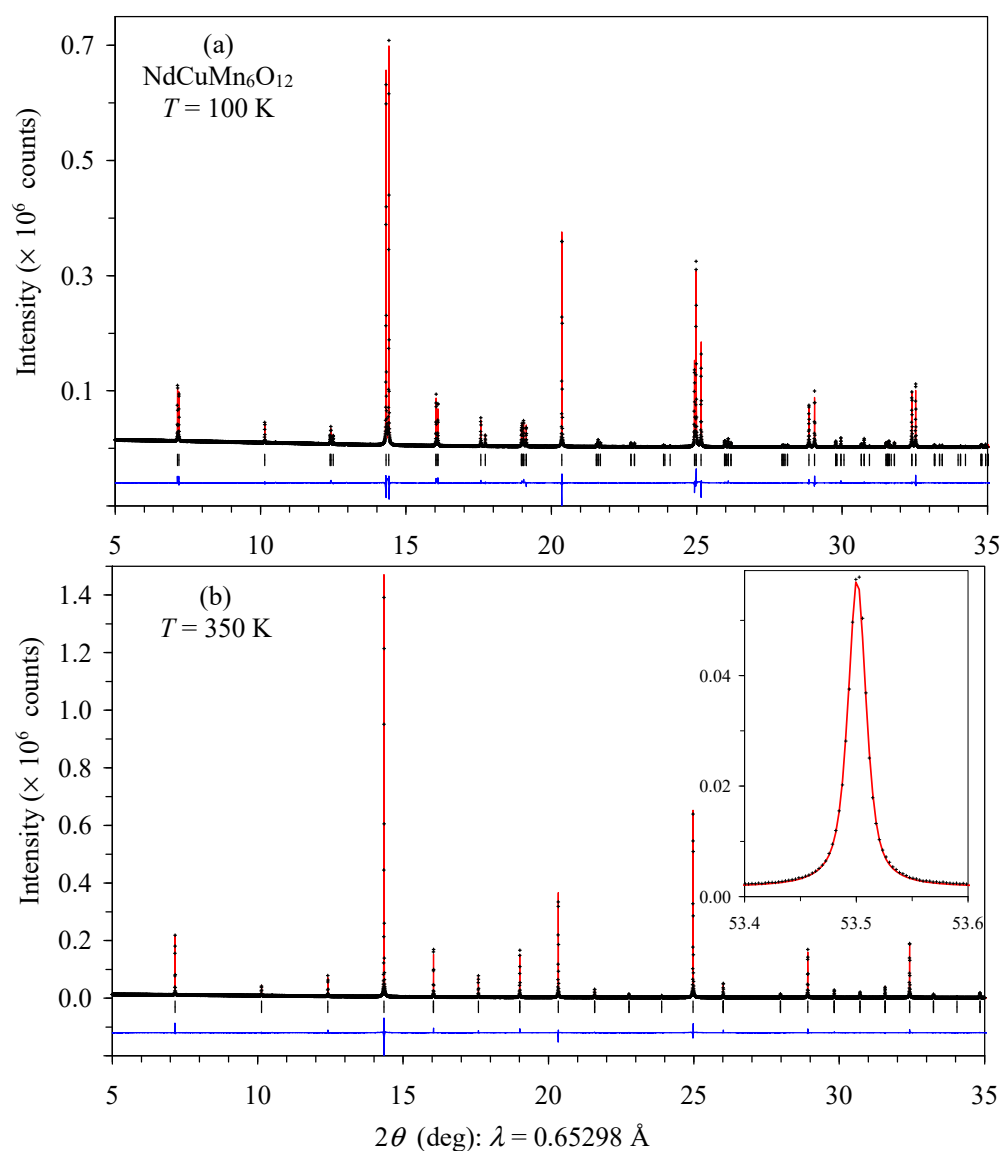


Figure 1. Fragments (between 5° and 35°) of experimental (black crosses), calculated (red line), and difference (blue line at the bottom) synchrotron powder X-ray diffraction patterns of $\text{NdCuMn}_6\text{O}_{12}$ at (a) $T = 100 \text{ K}$ in the $R\bar{3}$ phase and (b) $T = 350 \text{ K}$ in the $Im\bar{3}$ phase. The tick marks show possible Bragg reflection positions. The inset in (b) emphasizes the shape of reflections in the high 2θ region.

The crystal structures of $\text{NdCuMn}_6\text{O}_{12}$ were refined by the Rietveld method from synchrotron XRD data. The initial structural models were taken from $\text{CaMn}_7\text{O}_{12}$ [16]. Structural parameters of $\text{NdCuMn}_6\text{O}_{12}$ at some selected temperatures are summarized in Tables 1 and 2. Experimental, calculated, and difference synchrotron XRD patterns of $\text{NdCuMn}_6\text{O}_{12}$ at 100 K and 350 K are shown in Figure 1. In the cubic $Im\bar{3}$ modification,

reflections were very sharp and symmetrical (the inset of Figure 1b) indicating good crystallinity and homogeneity of the sample.

Table 1. Structure parameters of charge-ordered $\text{NdCuMn}_6\text{O}_{12}$ at selected temperatures from synchrotron X-ray powder diffraction data.

T (K)	100	150	200	250	270
<i>a</i> (Å)	10.48252 (1)	10.48518 (1)	10.48747 (1)	10.48916 (1)	10.48927 (1)
<i>c</i> (Å)	6.35552 (1)	6.35415 (1)	6.35544 (1)	6.35884 (1)	6.36119 (1)
<i>V</i> (Å ³)	604.8011 (7)	604.9781 (6)	605.3652 (7)	605.8845 (7)	606.1211 (8)
<i>B</i> (Nd) (Å ²)	0.145 (7)	0.183 (6)	0.237 (7)	0.282 (7)	0.299 (7)
<i>B</i> (Mn1/Cu1) (Å ²)	0.390 (8)	0.421 (8)	0.478 (8)	0.555 (9)	0.585 (9)
<i>B</i> (Mn2) (Å ²)	0.147 (9)	0.164 (8)	0.192 (8)	0.232 (9)	0.242 (9)
<i>B</i> (Mn3) (Å ²)	0.136 (16)	0.149 (15)	0.169 (15)	0.204 (16)	0.218 (17)
<i>x</i> (O1)	0.2180 (2)	0.2181 (2)	0.2181 (2)	0.2181 (3)	0.2179 (3)
<i>y</i> (O1)	0.2671 (3)	0.2672 (2)	0.2672 (2)	0.2672 (3)	0.2671 (3)
<i>z</i> (O1)	0.0824 (3)	0.0821 (3)	0.0819 (3)	0.0823 (3)	0.0832 (3)
<i>B</i> (O1) (Å ²)	0.22 (4)	0.23 (4)	0.26 (4)	0.37 (4)	0.43 (4)
<i>x</i> (O2)	0.3425 (2)	0.3423 (2)	0.3423 (2)	0.3423 (2)	0.3423 (2)
<i>y</i> (O2)	0.5231 (2)	0.5231 (2)	0.5231 (2)	0.5230 (2)	0.5229 (2)
<i>z</i> (O2)	0.3442 (4)	0.3441 (4)	0.3439 (3)	0.3440 (4)	0.3438 (4)
<i>B</i> (O2) (Å ²)	0.27 (4)	0.26 (4)	0.27 (4)	0.35 (4)	0.39 (4)
<i>R</i> _{wp} (%)	5.54	5.31	5.25	5.46	5.78
<i>R</i> _p (%)	3.58	3.50	3.47	3.57	3.77
<i>R</i> _B (%)	3.09	3.06	3.07	3.16	3.25

Source: Synchrotron powder X-ray diffraction ($\lambda = 0.65298$ Å); used *d*-space range: 0.6595–7.485 Å (measured *d*-space range: 0.6595–12.273 Å). Crystal system: trigonal. Space group *R*-3 (No. 148, hexagonal axes), *Z* = 3. Nd cations occupy the 3*a* site (0, 0, 0); Mn1/Cu1—9*e* site (0.5, 0, 0); Mn2—9*d* site (0.5, 0, 0.5); Mn3—3*b* site (0, 0, 0.5); O3 and O4—18*f* site (*x*, *y*, *z*). The occupation factors of the Nd, Mn2, Mn3, O1, and O2 sites are 1; the occupation of the Mn1/Cu1 site is 2/3Mn + 1/3Cu.

Table 2. Structure parameters of charge-disordered $\text{NdCuMn}_6\text{O}_{12}$ at selected temperatures from synchrotron X-ray powder diffraction data.

T (K)	310	350
<i>a</i> (Å)	7.39512 (1)	7.39722 (1)
<i>V</i> (Å ³)	404.4227 (2)	404.7675 (2)
<i>B</i> (Nd) (Å ²)	0.402 (6)	0.429 (5)
<i>B</i> (Mn1/Cu1) (Å ²)	0.801 (9)	0.832 (8)
<i>B</i> (Mn2) (Å ²)	0.332 (7)	0.348 (6)
<i>y</i> (O)	0.30559 (18)	0.30573 (16)
<i>z</i> (O)	0.17458 (20)	0.17457 (17)
<i>B</i> (O) (Å ²)	0.51 (3)	0.58 (3)
<i>R</i> _{wp} (%)	6.37	5.46
<i>R</i> _p (%)	4.03	3.71
<i>R</i> _B (%)	4.77	4.13

Source: Synchrotron powder X-ray diffraction ($\lambda = 0.65298$ Å); used *d*-space range: 0.6595–7.485 Å (measured *d*-space range: 0.6595–12.273 Å). Crystal system: cubic. Space group *Im*-3 (No. 204), *Z* = 2. Nd cations occupy the 2*a* site (0, 0, 0); Mn1/Cu1—6*b* site (0, 0.5, 0.5); Mn2—8*c* site (0.25, 0.25, 0.25); O—24*g* site (0, *y*, *z*). The occupation factors of the Nd, Mn2, and O sites are 1; the occupation of the Mn1/Cu1 site is 2/3Mn + 1/3Cu.

In the crystal structure analysis, Cu^{2+} cations were placed at the square-planar A' site (together with Mn^{3+} cations) with a fixed occupation as 2/3Mn + 1/3Cu for the Mn1/Cu1 site. Previous structural studies of similar compounds with neutron powder diffraction (which can easily distinguish between Cu and Mn) showed that Cu^{2+} cations are always located at the A' site due to the strong JT effect of Cu^{2+} cations [25,37,41,47,53,54]. For

unknown reasons, the available synchrotron XRD data were not so sensitive to the location of Cu^{2+} cations in $\text{NdCuMn}_6\text{O}_{12}$ even though the Cu^{2+} and Mn^{3+} cations differ by five electrons (or about 20%). For example, the refined occupation factor of the Mn1 site (when only Mn was placed at this site) was $g(\text{Mn1}) = 1.036(1)$ with refined $B = 0.67(9) \text{ \AA}^2$ (using the 350 K data in the cubic modification because of the lower number of refined parameters). The obtained g value was within the sensitivity of the method (that is, not noticeably higher) as a similar value was obtained for the Nd site when refined ($g(\text{Nd}) = 1.035(1)$ with refined $B = 0.497(6) \text{ \AA}^2$). $g(\text{Mn2})$ was refined to be $0.983(1)$ with refined $B = 0.289(8) \text{ \AA}^2$. Note that two other sets of synchrotron XRD data measured on different batches of $\text{NdCuMn}_6\text{O}_{12}$ (at $T = 380 \text{ K}$ with $\lambda = 0.65298 \text{ \AA}$) gave $g(\text{Nd}) = 1.015(1)$, $g(\text{Mn1}) = 1.045(2)$, and $g(\text{Mn2}) = 1.000(2)$, and $g(\text{Nd}) = 1.024(1)$, $g(\text{Mn1}) = 1.044(1)$, and $g(\text{Mn2}) = 1.014(1)$. In all cases, the occupation factor of the Mn1 site was slightly larger than that of the Mn2 site (when only Mn was placed at these sites).

Figure 2 shows the temperature dependence of the lattice parameters obtained from laboratory and synchrotron XRD data (see also Tables S1 and S2). Note that the lattice parameters of the $R\text{-}3$ modification were transformed from the hexagonal axes ($a_{\text{H}} \approx 10.5 \text{ \AA}$ and $c_{\text{H}} \approx 6.36 \text{ \AA}$) to the rhombohedral axes ($a_{\text{R}} \approx 6.42 \text{ \AA}$ and $\alpha_{\text{R}} \approx 109.6^\circ$; $a_{\text{R}} = (a_{\text{H}} \times \beta)/3$, $\alpha_{\text{R}} = 2 \times \arcsin(1.5/\beta)$, $\beta = (3 + (c_{\text{H}}/a_{\text{H}})^2)^{1/2}$) and then to a different cell choice in the rhombohedral axes ($a_{\text{R}} \approx 7.40 \text{ \AA}$ and $\alpha_{\text{R}} \approx 90.3^\circ$) for the better comparison with the cubic $Im\text{-}3$ modification ($a_{\text{C}} \approx 7.40 \text{ \AA}$ (and $\alpha_{\text{C}} = 90^\circ$)). The two phases co-existed in a certain temperature range near RT indicating a phase transition of the first order. There were some differences in the a_{R} parameter for the laboratory and synchrotron XRD data. These differences can be explained by different zero-shift parameters for different XRD sources (zero-shift parameters are usually very small for synchrotron XRD data) and by the fact that samples from different batches were used for the laboratory and synchrotron XRD measurements. The a_{R} parameter gradually decreases with decreasing temperature and then becomes nearly temperature-independent below about 100 K. The rhombohedral angle α_{R} shows a dome-like behavior between $T_{\text{CO}} (\approx 292 \text{ K})$ and 60 K, and its temperature behavior changes below 50 K, where it slightly decreases with decreasing temperature. No anomalies in the lattice parameters were observed at the first magnetic transition temperature ($T_{\text{C}} = 120 \text{ K}$, see below). The $R\text{-}3$ modification was found to be stable below T_{CO} down to 5 K since no (new) modulation reflections were observed on laboratory XRD data down to 5 K and on high-resolution, high-intensity synchrotron XRD data down to 100 K within the sensitivity of both methods. Therefore, the structural behavior of $\text{NdCuMn}_6\text{O}_{12}$ is different from that of $\text{CaMn}_7\text{O}_{12}$ [10,16–19] below T_{CO} .

Figure 3 shows the temperature dependence of the bond lengths in $\text{NdCuMn}_6\text{O}_{12}$ in the $R\text{-}3$ and $Im\text{-}3$ modifications. The $Im\text{-}3$ modification has one crystallographic site for octahedral Mn cations. Therefore, this site should have an average oxidation state of +3.25. The bond-valence sum [55] value of +3.35 (at 350 K) supports the average value (for calculations we used $R_0 = 1.76$ for all Mn). The $R\text{-}3$ modification has two crystallographic sites for octahedral Mn cations. One octahedral site (Mn3) has short Mn-O distances (which are all the same and, therefore, the octahedral distortion parameter is zero). Therefore, this site should be occupied by Mn^{4+} . The bond-valence sum [55] value of +3.87 (at 270 K) supports this assignment. For the second octahedral site (Mn2), the MnO_6 octahedra have an apically compressed geometry with four longer Mn-O distances and two shorter Mn-O distances (and the resulting octahedral distortion parameter was about 8.4×10^{-4}). Such distortions are caused by the JT effect. This site should be occupied by Mn^{3+} , and the bond-valence sum [55] value of +3.20 (at 270 K) supports this assignment. The same structural features take place in $\text{CaMn}_7\text{O}_{12}$ [16] below T_{CO} . The bond-valence sum [55] values of the Nd sites remain nearly the same (+3.20 to +3.23) in the $R\text{-}3$ and $Im\text{-}3$ modifications. The larger values

than expected indicate that Nd^{3+} cations are overbonded, and this fact could be a reason why $\text{NdMn}_7\text{O}_{12}$ [51] and $\text{NdCuMn}_6\text{O}_{12}$ need a high-pressure high-temperature method for their preparation. The bond lengths remain nearly the same at all temperatures (except in the vicinity of T_{CO}). Therefore, the bond-valence sum values remain nearly constant at different temperatures. We note that the degree of charge separation [56] estimated by bond-valence sum calculations (about 66% in our case at 270 K) is always below ideal values as emphasized in the literature [23,56], and bond-valence calculations just indicate tendencies. The main reason seems to be the nature of bond-valence calculations as they are based on some average parameters obtained from the statistical analysis of many reported crystal structures. In principle, bond-valence parameters can be adjusted for specific materials and coordination numbers and environments. For example, in $\text{R}^{3+}\text{MnO}_3$ perovskites, where Mn definitely has the fixed oxidation state of +3 and strong JT distortions, the standard bond-valence calculations (with $R_0(\text{Mn}^{3+}) = 1.76$ [55]) give values from +3.12 to +3.21 even when structural parameters determined from neutron diffraction (with precise localization of oxygen atoms) are used [57]. The use of $R_0(\text{Mn}^{3+}) = 1.74$ gives bond-valence sums close to +3.0 in RMnO_3 perovskites and in the Mn2 site of $\text{NdCuMn}_6\text{O}_{12}$ (for the R-3 modification).

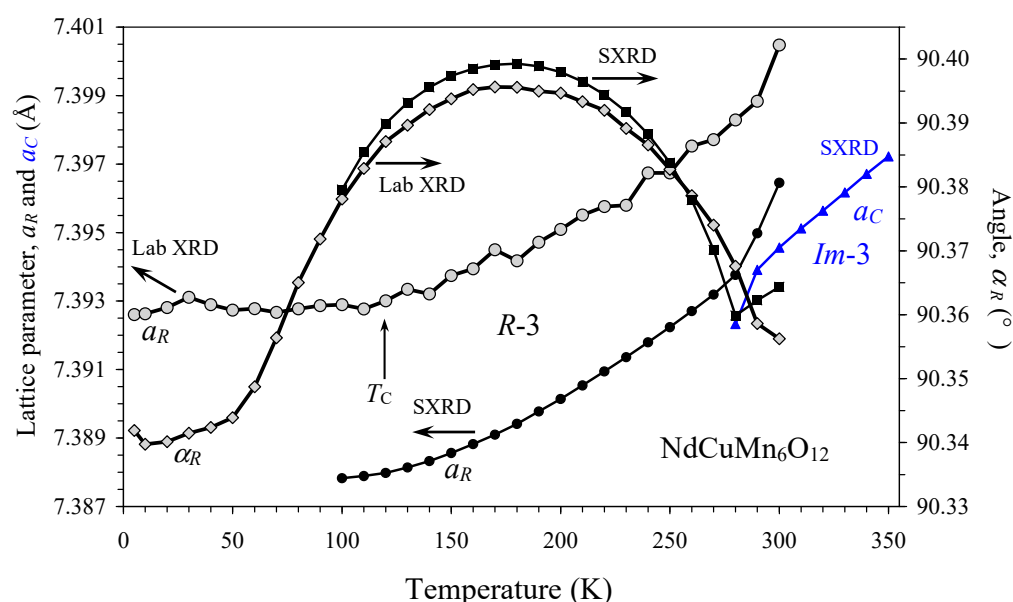


Figure 2. Temperature dependence of the lattice parameters of $\text{NdCuMn}_6\text{O}_{12}$ on heating. The left-hand axis shows the rhombohedral (a_R) and cubic (a_C) lattice parameter. The right-hand axis shows the rhombohedral angle (α_R). Black and blue symbols show results from synchrotron powder X-ray diffraction (SXR) measurements; gray symbols show results from laboratory powder X-ray diffraction (Lab XRD) measurements. The vertical arrow shows the position of the magnetic transition temperature, T_C .

The Mn-O bond lengths in $\text{NdCuMn}_6\text{O}_{12}$ in the R-3 modification are nearly temperature-independent (Figure 3). Therefore, the unusual JT distortions in $\text{NdCuMn}_6\text{O}_{12}$ do not experience any relaxation in comparison with $\text{CaMn}_7\text{O}_{12}$ [10,16]. However, the rhombohedral distortions/angles (Figure 2) first increased with decreasing temperature from 292 K to about 180 K in $\text{NdCuMn}_6\text{O}_{12}$; then they reduced on further cooling from 180 K down to 60 K producing the dome-like behavior of the temperature dependence of the rhombohedral angle. Below 60 K, the rhombohedral distortion/angle is nearly locked. This behavior could be related to unusual JT distortions and their tendency to be relaxed.

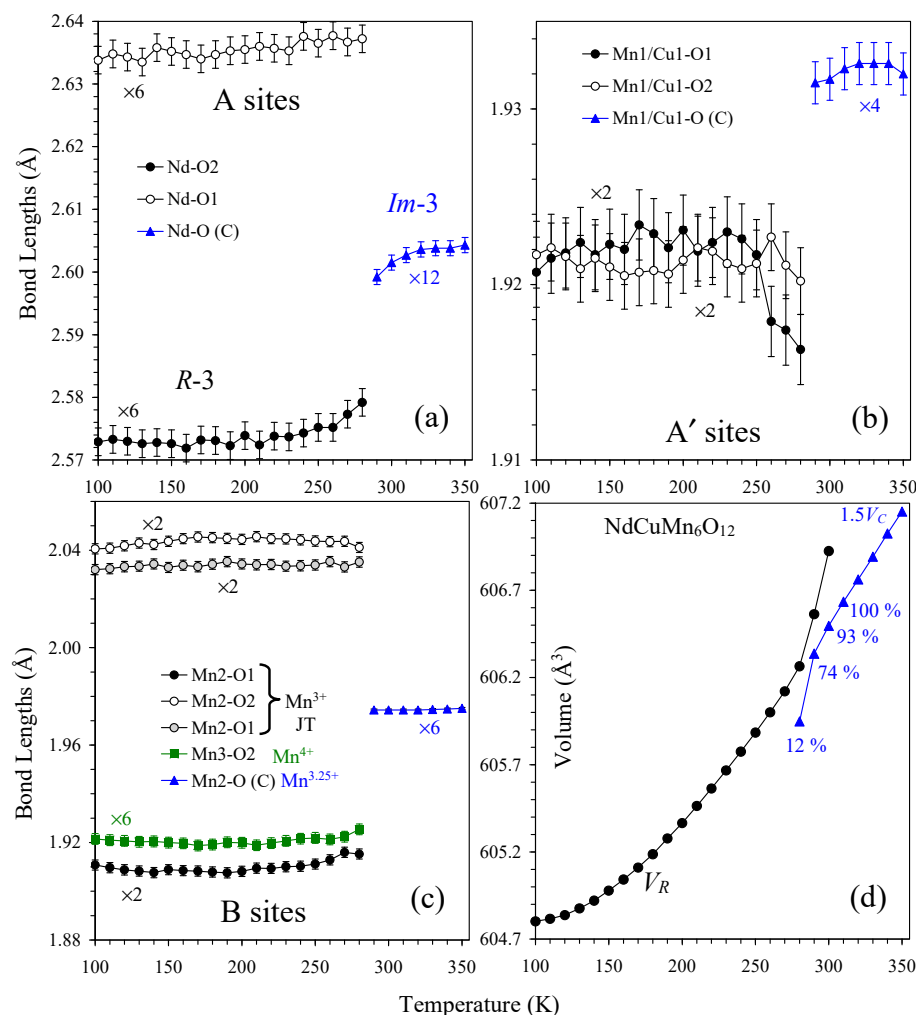


Figure 3. Temperature dependence of (a–c) bond lengths and (d) the (normalized to the *R*-3 cell) unit cell volume of NdCuMn₆O₁₂ on heating determined from synchrotron powder X-ray diffraction measurements. Data for the *Im*-3 phase are shown in blue. Numbers in (d) show the weight fraction of the cubic (C) *Im*-3 phase. The Nd-O bond lengths are given in (a), the Mn1/Cu1-O bond lengths for the square-planar site are given in (b), and the Mn-O bond lengths for the octahedral sites are given in (c).

Structural behavior of NdCuMn₆O₁₂ was also investigated with differential scanning calorimetry (DSC) (Figure 4). NdCuMn₆O₁₂ showed sharp and strong DSC anomalies on both heating and cooling curves confirming the presence of a structural phase transition with $T_{CO} = 292$ K (defined from peak positions on heating curves). DSC anomalies showed good reproducibility on cycling. The sample batch used in this study showed relatively strong and sharp DSC anomalies, and two peaks with nearly the same intensity were clearly resolved plus a shoulder was observed from a high-temperature side. This feature could indicate a phase separation, which was observed in NdCu_xMn_{7-x}O₁₂ solid solutions with $x = 0.1, 0.2$, and 0.3 [52]. However, high-resolution synchrotron XRD data (the inset of Figure 1b) did not detect any evidence of a phase separation. Other batches of NdCuMn₆O₁₂ samples showed broader and weaker DSC anomalies (Figures S1 and S2), and no evidence of a phase separation could be seen from such DSC data. Therefore, if a phase separation is present, it is quite small.

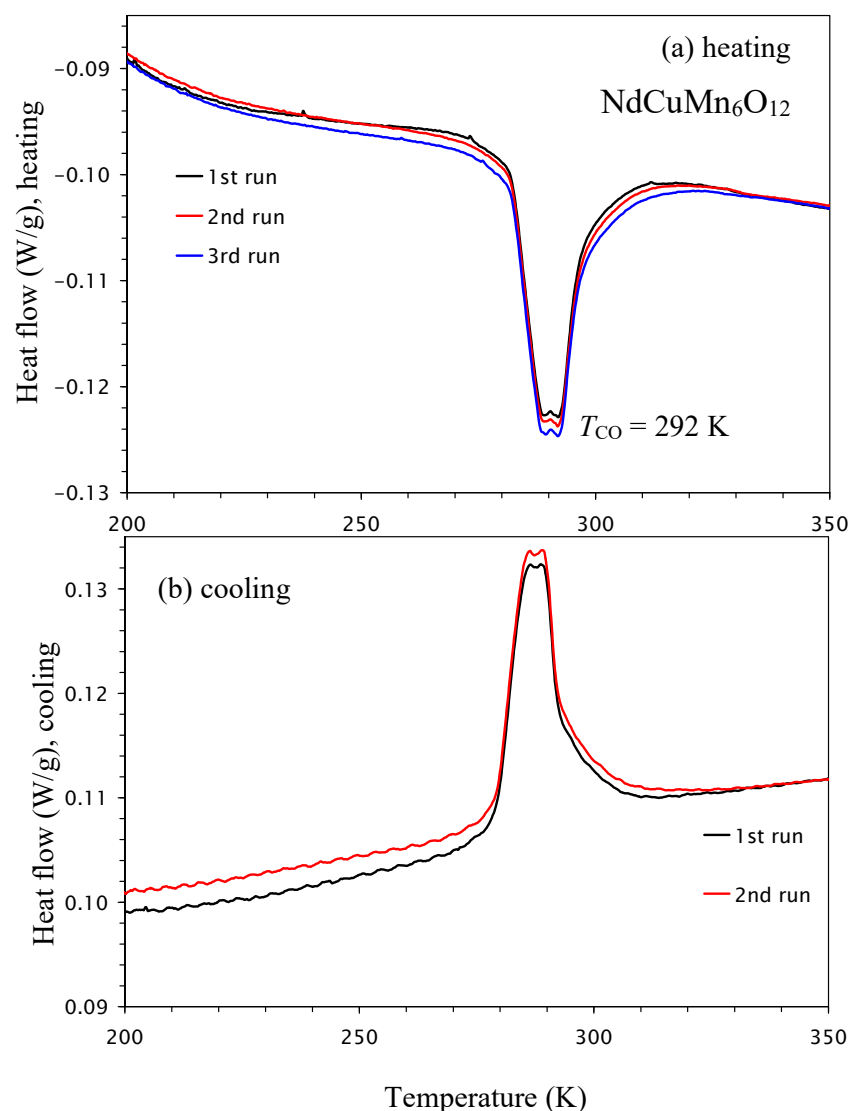


Figure 4. Differential scanning calorimetry (DSC) curves of NdCuMn₆O₁₂ (29.40 mg) during (a) heating and (b) cooling. Three DSC runs were performed (and shown) to check the reproducibility.

Figure 5 shows the direct current (dc) χ versus T curves of NdCuMn₆O₁₂ under magnetic fields $H = 100$ Oe and 10 kOe. There were two clear anomalies (at $H = 100$ Oe). The first strong anomaly was observed on both zero-field-cooled (ZFC) and field-cooled on cooling (FCC) curves near $T_C = 120$ K due to a ferrimagnetic transition. T_C was defined from the peak positions on differential curves (Figure S3). The second anomaly (near $T_{N2} = 20$ K) was quite broadened and was observed as a kink on the ZFC curve and a gradual decrease on the FCC curve. No clear anomalies could be seen at a large magnetic field of $H = 10$ kOe. Neutron diffraction studies of the undoped NdMn₇O₁₂ showed that a gradual small decrease on χ versus T curves is correlated with a gradual increase in the ordered moments on the Nd³⁺ sublattice [50,51], and the Nd³⁺ sublattice orders antiferromagnetically with the ferrimagnetic structure formed by the Mn³⁺ sublattices [50]. However, we note that the decrease on χ versus T curves was observed in NdMn₇O₁₂ below $T_3 \sim 8$ K at higher magnetic fields (e.g., $H = 10$ kOe); at smaller magnetic fields (e.g., $H = 100$ Oe), the decrease already started below about 16 K. Therefore, we can assume that the second magnetic anomaly in NdCuMn₆O₁₂ also corresponds to the antiferromagnetic (AFM) ordering of the Nd³⁺ sublattice. A similar decrease in magnetic susceptibilities at low temperatures was observed in NdCu_{*x*}Mn_{7-*x*}O₁₂ solid solutions with $x = 1.5$ –3 [40,41]

and in $\text{NdCu}_3\text{Mn}_3\text{FeO}_{12}$ [58]. Neutron diffraction studies of $\text{NdCu}_3\text{Mn}_3\text{FeO}_{12}$ [58] also allowed suggesting AFM ordering of the Nd sublattice. However, a final conclusion about the origin of the low-temperature susceptibility drops at small magnetic fields and the second magnetic transition in $\text{NdCuMn}_6\text{O}_{12}$ can only be made from future neutron diffraction studies.

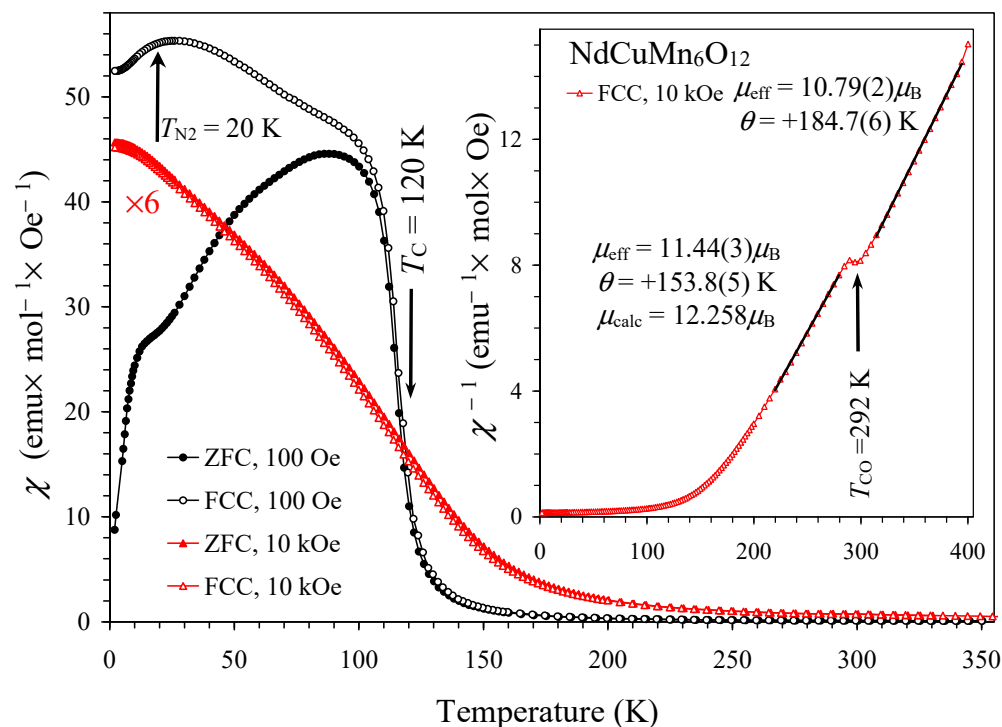


Figure 5. Magnetic properties of $\text{NdCuMn}_6\text{O}_{12}$. Zero-field-cooled (ZFC: filled curves) and field-cooled on cooling (FCC: empty curves) curves are shown at $H = 100$ Oe (black curves) and $H = 10$ kOe (red curves; multiplied by 6). The inset gives the inverse FCC χ^{-1} versus T curve at $H = 10$ kOe with Curie–Weiss fits (black lines) and fitting parameters in two regions. Vertical arrows emphasize the magnetic transition temperature (T_C) and the charge-order transition temperature (T_{CO}).

Magnetic anomalies were observed at the structural phase transition of $T_{CO} = 292$ K, where they could be clearly seen as a sharp step on the inverse magnetic susceptibilities (the inset of Figure 5). The Curie–Weiss law was applied to obtain effective magnetic moments and Curie–Weiss temperatures. We fitted the FCC inverse magnetic susceptibilities (at $H = 10$ kOe) in the temperature ranges of 220–270 K and 320–395 K. The fitting parameters are reported in Figure 5. The Curie–Weiss temperature was positive indicating the predominant ferromagnetic (FM) interactions between magnetic ions. The Curie–Weiss temperature was larger in the $Im\bar{3}$ modification in comparison with the $R\bar{3}$ modification, while the effective magnetic moment was larger for the $R\bar{3}$ modification and closer to the expected value of $12.258 \mu_B$ (for the calculation, we used $3.5 \mu_B$ for Nd^{3+} , $1.732 \mu_B$ for Cu^{2+} , $4.899 \mu_B$ for Mn^{3+} , and $3.873 \mu_B$ for Mn^{4+} [59]). Similar behavior of inverse magnetic susceptibilities was observed in $\text{PrCuMn}_6\text{O}_{12}$ [43], $\text{CeCuMn}_6\text{O}_{12}$ [44], and $\text{BiCuMn}_6\text{O}_{12}$ [53,54].

Isothermal magnetization curves (M versus H) at different temperatures are shown in Figures 6 and S4. They were typical for ferrimagnets with well-defined hysteresis near the origin. However, they did not fully saturate and showed gradual continuous increases in magnetization at higher magnetic fields indicating contributions from AFM interactions. The coercive field was about 600 Oe at $T = 2$ K, 200 Oe at $T = 5$ K, and ~ 0 Oe at $T = 20$ K. The magnetization values reached $\approx 17.8 \mu_B$ at $T = 2$ and 5 K (and at $H = 70$ kOe) and $\approx 17.3 \mu_B$ at $T = 20$ K. These values are close to the expected values with the FM interactions

between Cu^{2+} and all Mn^{3+} cations and AFM interactions with Mn^{4+} cations, $(1 + 20 - 3) = 18 \mu_B$ ($1 \mu_B$ is the maximum ordered moment of Cu^{2+} , $4 \mu_B$ is the maximum ordered moment of Mn^{3+} , and $3 \mu_B$ is the maximum ordered moment of Mn^{4+}). Contributions from Nd^{3+} can be neglected as the ordered moments of Nd^{3+} are usually below $1 \mu_B$ [50,58] and should be negligible at 20 K. In addition, similar saturation values were observed in $\text{CaCu}_x\text{Mn}_{7-x}\text{O}_{12}$ solid solutions with $1 \leq x \leq 2$ [34], which do not have magnetic rare-earth cations, and in $\text{NdCu}_x\text{Mn}_{7-x}\text{O}_{12}$ solid solutions with $x = 1.5$ and 2 [40]. $\text{RCu}_x\text{Mn}_{7-x}\text{O}_{12}$ and $\text{CaCu}_x\text{Mn}_{7-x}\text{O}_{12}$ solid solutions have a tendency to show saturation behavior for large Cu contents and gradual continuous increases in magnetization for smaller Cu contents, such as $x = 1$ [34,40,44,47].

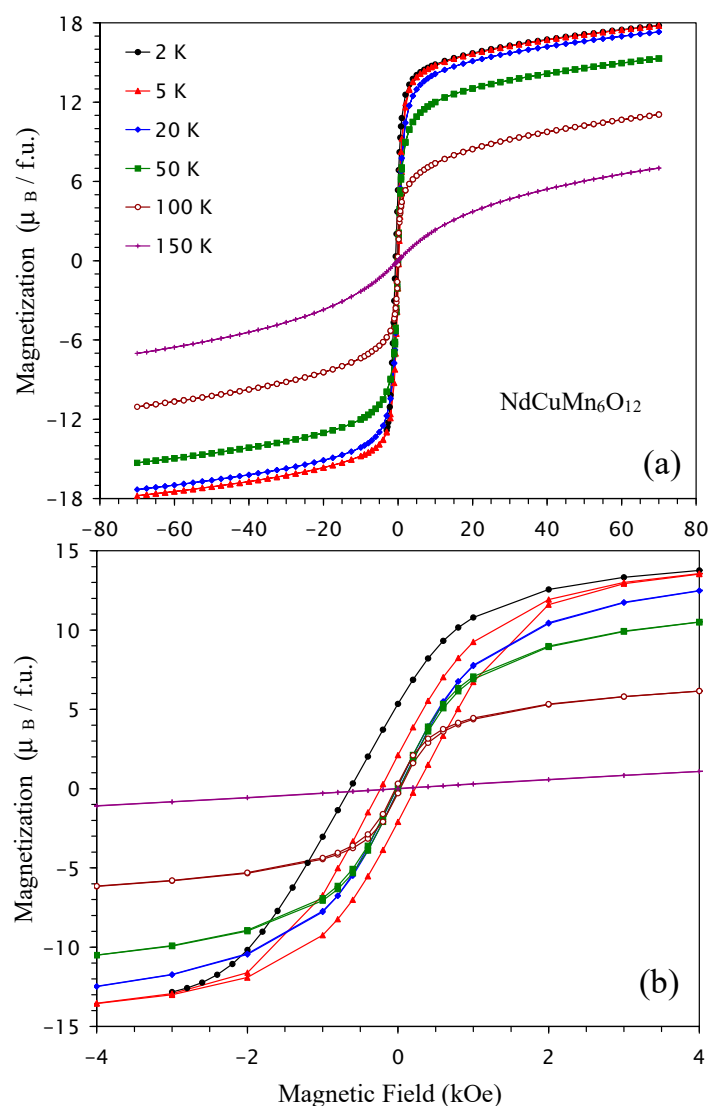


Figure 6. Magnetic properties of $\text{NdCuMn}_6\text{O}_{12}$: M versus H curves at $T = 2, 5, 20, 50, 100$, and 150 K. Panel (a) shows the full M versus H curves, panel (b) shows the zoomed-in M versus H curves near the origin.

Specific heat measurements (Figures 7 and S5) showed a very weak anomaly at $T_C = 120$ K (the inset of Figure 7), while a stronger anomaly was found near $T_{N2} = 20$ K. Specific heat data unambiguously confirmed the presence of the second magnetic transition. Magnetic fields slightly suppressed specific heat anomalies at T_{N2} and completely smeared anomalies at T_C and moved magnetic entropy to much higher temperatures. Such effects (near T_C) are typical for FM and ferrimagnetic materials.

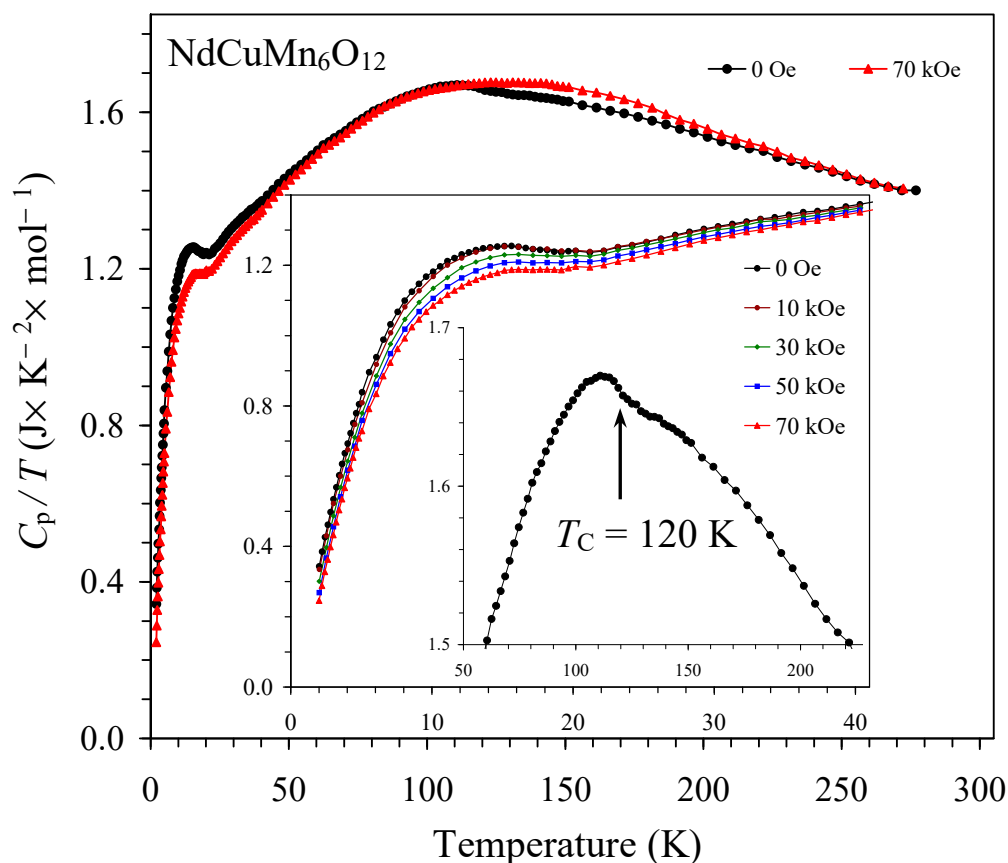


Figure 7. Specific heat data of $\text{NdCuMn}_6\text{O}_{12}$ plotted as C_p/T versus T at $H = 0$ Oe (black) and 70 kOe (red). The main inset shows the C_p/T versus T curves at $H = 0, 10, 30, 50$, and 70 kOe below 40 K. The second inset emphasizes specific heat anomalies near T_C at $H = 0$ Oe.

Ac susceptibility measurements were performed to get more information about the magnetic properties of $\text{NdCuMn}_6\text{O}_{12}$ (Figures 8, 9 and S6). Ac susceptibility curves were measured at different frequencies (Figure 8) and different ac fields (Figure 9). Some frequency dependence was observed on the χ' versus T curves between about 60 and 110 K, while much stronger frequency dependence was observed on the χ'' versus T curves between about 20 and 120 K. However, such frequency dependence was not caused by any spin-glass contributions; it was caused by interactions of the ac field with ferrimagnetic domain structures. Non-linear behavior (and the presence of interactions with domain structures) could be more clearly seen from the dependence on the ac field (Figure 9). The χ' versus T curves showed sharp decreases below about 16 K with the appearance of peaks on the χ'' versus T curves near 8–9 K. Anomalies below 20 K showed no dependence on the ac field, indicating the linear response. We note that very similar anomalies were observed below about 20 K in other members of the $\text{RCuMn}_6\text{O}_{12}$ series (for example, with $R = \text{Ce}, \text{Sm}$, and Dy [44]) especially on the χ'' versus T curves. Therefore, their origin could be unrelated to rare-earth elements (Nd in this case) and to the presence of the second magnetic transition in $\text{NdCuMn}_6\text{O}_{12}$ at T_{N2} .

The synthesis of $\text{NdCuMn}_6\text{O}_{12}$ was attempted in Ref. [41]. However, because of the presence of large amounts of Mn-containing impurities (NdMn_2O_5 and Mn_2O_3), the composition of the main perovskite phase was shifted to the Cu-rich side. As a result, the main perovskite phase remained cubic down to 5 K, and no structural phase transitions were observed. In addition, the magnetic transition temperature was observed at a noticeably higher temperature of 206 K in Ref. [41] (in comparison with 120 K for our sample); our estimation shows that such a transition corresponds to a $\text{NdCu}_{1.4}\text{Mn}_{5.6}\text{O}_{12}$

composition. Our sample was single-phase, suggesting that the target composition was achieved, and our sample showed a structural transition from $Im\bar{3}$ symmetry (at high temperatures) to $R\bar{3}$ symmetry near 292 K. Such a structural transition was observed at 267 K in $\text{PrCuMn}_6\text{O}_{12}$ [43], at 297 K in $\text{CeCuMn}_6\text{O}_{12}$ [44], and at 296 K in $\text{BiCuMn}_6\text{O}_{12}$ [53,54].

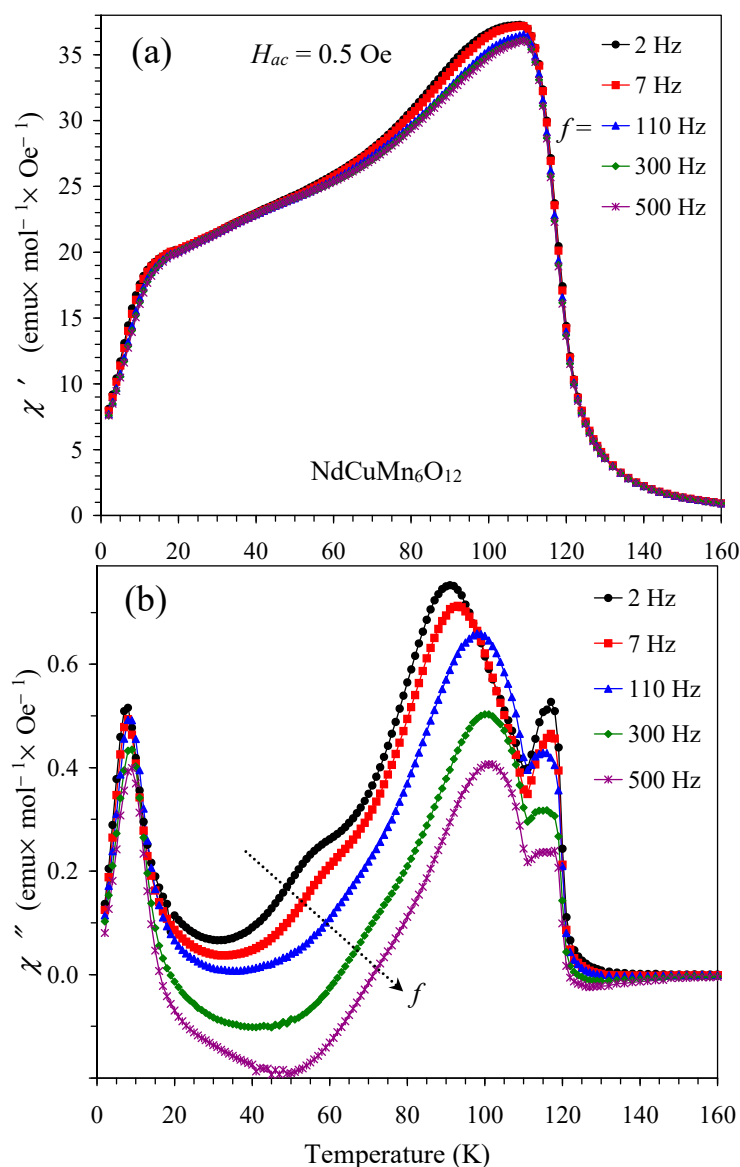


Figure 8. (a) The χ' versus T and (b) χ'' versus T curves of $\text{NdCuMn}_6\text{O}_{12}$ at different frequencies ($f = 2, 7, 110, 300, 500$ Hz) measured with $H_{ac} = 0.5$ Oe and $H_{dc} = 0$ Oe.

$\text{AA}'_3\text{Mn}_4\text{O}_{12}$ -type perovskites with the 1:3 ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$ cations at the B sites show CO structural transitions from $Im\bar{3}$ symmetry (at high temperatures) to $R\bar{3}$ symmetry and compressed Mn^{3+}O_6 octahedra in the average structure of the $R\bar{3}$ modification, which is sometimes called an orbital disorder phase [23]. Relaxation of compressed Mn^{3+}O_6 octahedra occurs through different mechanisms on further cooling [10]. As mentioned in the introduction, $\text{AMn}_7\text{O}_{12}$ compounds with $A = \text{Ca}, \text{Sr}, \text{and Pb}$ show incommensurately modulated structures, where Mn^{3+}O_6 octahedra become locally elongated [10,20]. $\text{CdMn}_7\text{O}_{12}$ shows a commensurately modulated structure (space group $P\bar{3}$), where a part of Mn^{3+}O_6 octahedra restores their typical JT distortions [10,20]. $\text{HgMn}_7\text{O}_{12}$ shows a polar orthorhombic distortion (space group $Pnn2$), an additional charge transfer, and the restoration of typical JT distortions of Mn^{3+}O_6 octahedra [23]. $\text{BiCuMn}_6\text{O}_{12}$ shows a

unique re-entrant structural transition, where the $R\text{-}3$ modification collapses back to the cubic $Im\text{-}3$ modification on cooling [53,54]. $\text{CeCuMn}_6\text{O}_{12}$ demonstrated a phase separation below about 80 K [44]. Therefore, the apparent absence of any further structural transitions in $\text{NdCuMn}_6\text{O}_{12}$ may need a deeper understanding and further detailed structural characterizations at low temperatures, including more sensitive methods such as electron and neutron diffraction.

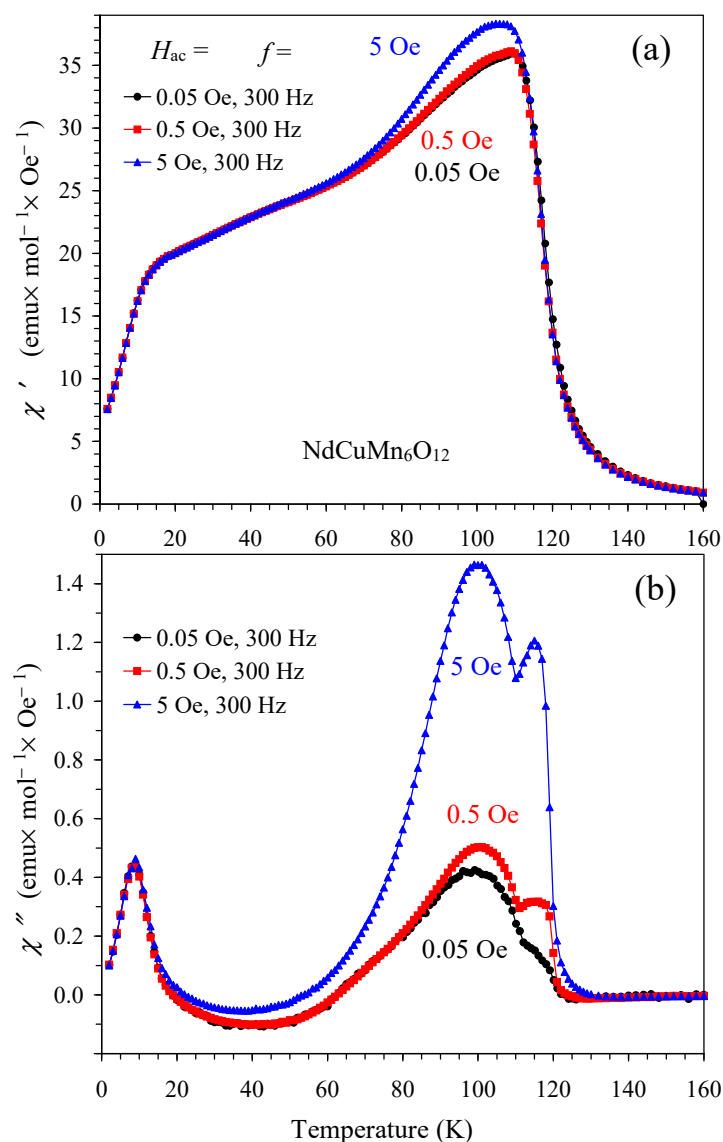


Figure 9. (a) The χ' versus T and (b) χ'' versus T curves of $\text{NdCuMn}_6\text{O}_{12}$ at different $H_{ac} = 0.05, 0.5$, and 5 Oe and one frequency of 300 Hz (under $H_{dc} = 0$ Oe).

3. Materials and Methods

$\text{NdCuMn}_6\text{O}_{12}$ samples were prepared from stoichiometric mixtures of Nd_2O_3 (Rare Metallic Co., Tokyo, Japan, 99.9%), CuO (Rare Metallic Co., Tokyo, Japan, 99.9%), MnO_2 (Alfa Aesar, Ward Hill, MA, USA, 99.99%), and Mn_2O_3 . Single-phase Mn_2O_3 was prepared from a commercial MnO_2 chemical (Rare Metallic Co., Tokyo, Japan, 99.99%) by annealing in air at 923 K for 24 h. The synthesis was performed at 6 GPa and at 1600 K for 2 h in sealed Pt capsules using a belt-type high-pressure (HP) instrument. After annealing at 1600 K, the samples were cooled down to room temperature (RT) by turning off the heating current, and the pressure was slowly released.

Laboratory powder X-ray diffraction (XRPD) data were collected at RT on a Mini-Flex600 diffractometer (Rigaku, Tokyo, Japan) using $\text{CuK}\alpha$ radiation (2θ range of 10 – 80° , a step width of 0.02° , and scan speed of $2^\circ/\text{min}$). Low-temperature laboratory XRPD data were measured on a RIGAKU SmartLab instrument ($\text{CuK}\alpha_1$ radiation at 45 kV and 200 mA; 2θ range of 10 – 110° , a step width of 0.02° , and scan speed of $1^\circ/\text{min}$) from 5 K to 300 K (Bragg–Brentano geometry was used for all laboratory XRPD). Synchrotron XRPD data were measured on the BL15XU beamline (the former NIMS beamline) of SPring-8 [60] between 3.05° and 59.35° at 0.003° intervals in 2θ with the wavelength of $\lambda = 0.65298 \text{ \AA}$ from 100 K to 350 K. The sample was placed into an open Lindemann glass capillary tube (inner diameter: 0.1 mm), which was rotated during measurements. The Rietveld analysis of all XRPD data was performed using the RIETAN-2000 program [61].

Magnetic measurements were performed on a SQUID magnetometer (Quantum Design MPMS-XL-7T, San Diego, CA, USA) between 2 K and 350–400 K in applied fields of 100 Oe and 10 kOe under both zero-field-cooled (ZFC) and field-cooled on cooling (FCC) conditions. Magnetic-field dependence was measured at different temperatures between -70 and 70 kOe. Frequency-dependent alternating current (ac) susceptibility measurements were performed on cooling with a MPMS-1T instrument (Quantum Design, San Diego, CA, USA) at zero static dc field and at different frequencies (f) and different applied oscillating magnetic fields (H_{ac}).

Specific heat, C_p , was measured on cooling from 270 K to 2 K at zero magnetic field and 70 kOe and from 40 K to 2 K at $H = 10, 30$, and 50 kOe by a pulse relaxation method using a commercial calorimeter (Quantum Design PPMS, San Diego, CA, USA). All magnetic and specific heat measurements were performed using pieces of pellets.

Differential scanning calorimetry (DSC) curves of a powder sample (29.40 mg) were recorded on a Mettler Toledo DSC1 STAR^e system (Columbus, OH, USA) between 173 K and 423 K in open Al capsules with a heating/cooling rate of 10 K/min. Three DSC runs were performed to check the reproducibility.

All the above measurements (except low-temperature laboratory XRPD because such an experiment required a relatively large amount of a sample) were performed using the same batch of the prepared sample.

4. Conclusions

In conclusion, the A-site-ordered quadruple perovskite $\text{NdCuMn}_6\text{O}_{12}$, with the presence of $\text{Mn}^{4+}/\text{Mn}^{3+}$ cations with the 1:3 ratio at the B perovskite sites and therefore resembling $\text{CaMn}_7\text{O}_{12}$, was prepared by a high-pressure high-temperature method. A first-order structural phase transition from $Im\bar{3}$ symmetry (at high temperatures) to $R\bar{3}$ symmetry was found near $T_{\text{CO}} = 292 \text{ K}$ accompanied by charge ordering and orbital ordering with unusual apically compressed Jahn–Teller distortions of MnO_6 octahedra. In comparison with $\text{CaMn}_7\text{O}_{12}$, no additional structural transitions were found in $\text{NdCuMn}_6\text{O}_{12}$ within the sensitivity of the used methods, indicating that compressed Jahn–Teller distortions were not relaxed. $\text{NdCuMn}_6\text{O}_{12}$ shows a ferrimagnetic transition below 120 K, and the second magnetic transition near 20 K was found in $\text{NdCuMn}_6\text{O}_{12}$.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics14070174/s1>, Figure S1 and Figure S2: Differential scanning calorimetry (DSC) curves of a different batch of $\text{NdCuMn}_6\text{O}_{12}$ on (a) heating and (b) cooling. Three DSC runs were performed (and shown) to check the reproducibility. The peaks were broader in comparison with a sample used in the main text. The inset on (b) shows the shape of cubic reflections ($6\bar{8}2$) and $(10\bar{2}0)$ of synchrotron XRD data (at $T = 380 \text{ K}$ with $\lambda = 0.65298 \text{ \AA}$) for this sample; axes: intensity (counts/ 10^6) versus 2θ ($^\circ$); Figure S3: Magnetic properties of $\text{NdCuMn}_6\text{O}_{12}$. (a) Zero-field-cooled (ZFC: filled curves) and field-cooled on cooling (FCC: empty curves) curves are shown at

$H = 5$ Oe (black curves). A different (compared with the main text) FCC curve at $H = 100$ Oe is shown in blue. The inset shows differential curves, $d\chi/dT$ versus T . (b) The ZFC and FCC $d\chi/dT$ versus T curves at $H = 10$ kOe (red curves); Figure S4: Magnetic properties of $\text{NdCuMn}_6\text{O}_{12}$: M versus H curves at $T = 150, 200, 250$, and 300 K; Figure S5: Specific heat data of $\text{NdCuMn}_6\text{O}_{12}$ (the same batch as used in the main text) in a high-temperature region plotted as C_p versus T (the left-hand axis) and C_p/T versus T (the right-hand axis) at $H = 0$ Oe on heating (red and pink) and cooling (blue) with a step of 2 K. An H Apiezon grease was used for a better thermal contact between the sample and a sample holder. An addenda contribution was measured with a step of 4 K. Specific heat measurements are in agreement with the DSC measurements (Figure 4) and show a double-peak feature; Figure S6: (a) The χ' versus T and (b) χ'' versus T curves of a different batch of $\text{NdCuMn}_6\text{O}_{12}$ at different frequencies ($f = 2, 7, 25, 110, 500$ Hz) measured with $H_{ac} = 0.5$ Oe and $H_{dc} = 0$ Oe using MPMS3; Table S1 and Table S2: Numerical data used to plot Figure 2.

Author Contributions: Conceptualization, A.A.B.; methodology, A.A.B.; validation, A.A.B.; formal analysis, A.A.B.; investigation, A.A.B., R.L., L.Z., Y.M. and K.Y.; resources, K.Y.; data curation, A.A.B.; writing—original draft preparation, A.A.B.; writing—review and editing, A.A.B.; supervision, A.A.B. and K.Y.; project administration, A.A.B.; funding acquisition, K.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This work was partially supported by a Grant-in-Aid for Scientific Research (No. JP25K01657) from the Japan Society for the Promotion of Science.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Materials. Further inquiries can be directed to the corresponding author.

Acknowledgments: The synchrotron radiation experiments were conducted at the former NIMS beamline (BL15XU) of SPring-8 with the approval of the former NIMS Synchrotron X-ray Station (proposal numbers: 2016B4504, 2019B4500, and 2020A4501). We thank M. Tanaka and Y. Katsuya for their help at SPring-8. MANA was supported by the World Premier International Research Center Initiative (WPI), MEXT, Japan.

Conflicts of Interest: The authors declare no conflicts of interest.

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