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Structural and magnetic investigations of single-crystalline neodymium zirconate pyrochlore Nd$_2$Zr$_2$O$_7$

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We report structural and magnetic properties studies of large high-quality single crystals of the frustrated magnet Nd$_2$Zr$_2$O$_7$. Powder x-ray diffraction analysis confirms that Nd$_2$Zr$_2$O$_7$ adopts the pyrochlore structure. Room-temperature x-ray diffraction and time-of-flight neutron-scattering experiments show that the crystals are stoichiometric in composition with no measurable site disorder. The temperature dependence of the magnetic susceptibility shows no magnetic ordering at temperatures down to 0.5 K. Fits to the magnetic susceptibility data using a Curie-Weiss law reveal a ferromagnetic coupling between the Nd moments. Magnetization versus field measurements show a local Ising anisotropy along the (111) axes of the Nd$^{3+}$ ions in the ground state. Specific heat versus temperature measurements in zero applied magnetic field indicate the presence of a thermal anomaly below $T$ $\sim$ 7 K, but no evidence of magnetic ordering is observed down to 0.5 K. The experimental temperature dependence of the single-crystal bulk dc susceptibility and isothermal magnetization are analyzed using crystal field theory and the crystal field parameters and exchange coupling constants determined.

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I. INTRODUCTION

Pyrochlore oxides of the type $A_2^{3+}B_2^{4+}O_7$ (where $A$ = trivalent rare earth, $B$ = tetravalent transition metal element) are geometrically frustrated magnets [1,2]. These compounds have a face-centered cubic structure, with the space group $Fd\bar{3}m$ (No. 227). Both the rare-earth atoms occupying the $A$ sites and the transition metal elements located on the $B$ sites form a pyrochlore lattice, a three-dimensional arrangement of corner-sharing tetrahedra, known to display the highest degree of geometrical frustration, resulting in the many unusual magnetic properties of these systems. Depending on the nature of the interaction between the magnetic ions ($A$ and/or $B$ cations), these systems can exhibit either spin ice [3,4], spin glass [5,6], or highly correlated quantum disordered spin liquid states [7], as well as long-range magnetic order [2].

One exciting avenue of research in this field has focused on systems where, due to a smaller magnetic moment on the trivalent rare-earth $A$ site, quantum fluctuations play an important role in controlling the low-temperature physics of the materials. Recent studies have pointed to the possibility of quantum spin liquid behavior (in which spin ice correlations exist at finite temperature, together with strong quantum effects) in a number of pyrochlore materials, including Tb$_2$Ti$_2$O$_7$ and Yb$_2$Ti$_2$O$_7$ [8–10].

The success of research on pyrochlores, and particularly the titanates, is due, in part, to the availability of large, high-quality single crystals of these materials. Single crystals of all the titanate pyrochlore family were successfully grown using the floating-zone technique [11–13] and their magnetic ground states and properties have been investigated in great detail. (See Refs. [1] and [2], and references therein.)

As the search for geometrically frustrated magnetic pyrochlores that exhibit quantum effects widens, the research community has turned its attention to the rare-earth zirconates, $A_2Zr_2O_7$ [14]. It has been shown that the rare-earth zirconates can be stabilized into two crystallographic structures: an ordered pyrochlore phase, for the first few elements of the lanthanide series (from lanthanum to gadolinium), or a disordered fluorite phase, for the other lanthanides [15,16]. In addition, these oxides undergo an order-disorder phase transition, from the pyrochlore to the fluorite structure [15,17]. The temperature at which the structural transition occurs is strongly dependent on the nature of the rare-earth element. In addition, the coexistence of both the fluorite and pyrochlore phases has been observed in some zirconates with complex compositions [18,19].

To date, due to the high melting point of the zirconates, a majority of the studies of the structural and magnetic properties of the zirconate pyrochlores have been performed on powder samples [20]. Recently, large single crystals of the Pr containing zirconate pyrochlore, Pr$_2$Zr$_2$O$_7$, have been grown by the floating-zone technique [21–23]. Studies of the magnetic properties have shown that the Pr$^{3+}$ ions in Pr$_2$Zr$_2$O$_7$ have a ground-state doublet with a local Ising anisotropy along (111) axes and are coupled by an antiferromagnetic exchange, but no long-range magnetic order is observed down to very low temperatures (76 mK) [21,24,25]. The spin ice-like correlations revealed by elastic magnetic neutron scattering, the broad excitation spectrum observed in the low-energy range, and the large zero-field splitting present in these systems, make Pr$_2$Zr$_2$O$_7$ a promising candidate for a quantum spin liquid.
inelastic neutron scattering, and the reduction of the nuclear contribution to the heat capacity [24] may be connected with the strongly anisotropic superexchange and multipolar interactions [26,27] and interactions of the Pr$^{3+}$ ions with random lattice strains. (Strong sensitivity of the Pr$^{3+}$ ground state to lattice disorder in Pr$_2$−$x$Bi$_x$Ru$_2$O$_7$ pyrochlores was noted in Ref. [28].) Some possible low-temperature phases of the Pr$_2$Zr$_2$O$_7$ pyrochlore have been discussed recently in Ref. [10].

Neodymium zirconate, Nd$_2$Zr$_2$O$_7$, has been the subject of just a small number of studies (see, for example, Ref. [20]). A study of the phase diagram of Nd$_2$O$_3$−ZrO$_2$ shows that the pyrochlore oxide, Nd$_2$Zr$_2$O$_7$, melts congruently above 2000 °C, although the melting point was not established [29]. The order-to-disorder transition in Nd$_2$O$_3$−ZrO$_2$ occurs at 2300 °C [15,30], raising the possibility that it may be difficult to prepare Nd$_2$Zr$_2$O$_7$ single crystals of the pyrochlore structure due to the relatively small difference between the melting point and the structural transition temperature. When preparing this material it is therefore essential to establish the crystal structure and the structural transition temperature. When preparing this material it is therefore essential to establish the crystal structure and the structural transition temperature. When preparing this material it is therefore essential to establish the crystal structure and the structural transition temperature. When preparing this material it is therefore essential to establish the crystal structure and the structural transition temperature. When preparing this material it is therefore essential to establish the crystal structure and the structural transition temperature. When preparing this material it is therefore essential to establish the crystal structure and the structural transition temperature. When preparing this material it is therefore essential to establish the crystal structure and the structural transition temperature. When preparing this material it is therefore essential to establish the crystal structure and the structural transition temperature.
The Rietveld refinement method, with the FULLPROF software, is used for the refinement of the crystal structure. The results of the refinement for the cationic occupancy showed that the best model for the refinements is one in which there is no mixed occupancy of the cationic Zr sites.

B. Crystal structure

Room-temperature x-ray diffraction data were collected on small pieces of crystals that were powdered. The x-ray data were fitted to the cubic Fd3m space group [37] using the Rietveld refinement method, with the FULLPROF software suite [38]. The x-ray diffraction profile for the Nd2Zr2O7 crystal displayed in Fig. 1 shows no trace of any impurity and contains a number of weak superlattice reflections, demonstrating that the Fd3m pyrochlore structure is formed. These superlattice peaks, among which the strongest in the pattern are hkl = (111), (311), (331), and (511), indicate the cation and/or anion-vacancy ordering associated with the pyrochlore structure [16].

Attempts to fit the x-ray data using different models for the occupancies of the Nd and Zr sites showed that the best model for the refinements is one in which the occupancy of the oxygen 48f site is fixed to its nominal value of 1. The occupancy of the oxygen 8b site was fixed to the value of 1, as the oxygen vacancies are usually found to be mainly on the oxygen 48f site [39]. The occupancy of the oxygen 8b site was fixed to the value of 1, as the oxygen vacancies are usually found to be mainly on the oxygen 48f site [39].

The powder x-ray diffraction data measurements are sensitive to any preferred orientation present in the sample, and this is reflected in changes in the relative intensities of some of the Bragg peaks. In order to confirm the structural model obtained using the x-ray data using different models for the occupancies of the cation sites showed that there is no deficiency in Nd or Zr content, and no internal site disorder was detected in our Nd2Zr2O7 crystals. The best model for the refinement of the occupancies of the anion sites was found to be one in which only the O 48f site occupancy varies. Anisotropic thermal displacement parameters were used to refine the crystal structure. The structural parameters obtained from the best fit of the x-ray diffraction data at room temperature are listed in Table II.

In order to confirm the structural model obtained using the single-crystal XRD data, a small piece of an as-grown single crystal of Nd2Zr2O7 was cut from the boule and single-crystal time-of-flight neutron diffraction data were collected at room temperature. Attempts to fit the neutron data using different models for the occupancies of the Nd and Zr sites showed that the best model for the refinements is one in which the cationic occupancies are fixed to their nominal value of 1. The occupancy of the oxygen 8b site was fixed to the value of 1, as the oxygen vacancies are usually found to be mainly on the oxygen 48f site [39].

A summary of the results of the Rietveld refinement of the neutron diffraction data is given in Table III. The structural parameter was found to be slightly smaller than the previously reported value for polycrystalline samples [37]. Analysis of the room-temperature x-ray diffraction data collected on the powder used to prepare the feed rods showed that the calculated value of the lattice parameter (a = 10.682 87(5) Å) is, in this case, very similar to that reported in the literature [29,37].

The powder x-ray diffraction data were collected on a ground boule of Nd2Zr2O7. The experimental profile (red circles) and a Rietveld refinement (black line) made using the cubic Fd3m structure are shown, with the difference given by the blue line. The positions of the Bragg peaks are indicated by green vertical bars. The positions of the Bragg peaks are indicated by arrows.

![Fig. 1.](image)

**Figure 1.** Room-temperature powder x-ray diffraction pattern collected on a ground boule of Nd2Zr2O7. The experimental profile (red circles) and a Rietveld refinement (black line) made using the cubic Fd3m structure are shown, with the difference given by the blue line. The positions of the Bragg peaks are indicated by green vertical bars. The positions of the Bragg peaks are indicated by arrows.

### Table I. Crystallographic parameters for Nd2Zr2O7 refined using room-temperature powder x-ray diffraction data.

<table>
<thead>
<tr>
<th>Structural data</th>
<th>Cubic</th>
<th>Fd3m</th>
<th>a (Å)</th>
<th>10.62657(7)</th>
</tr>
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<tbody>
<tr>
<td>Rwp</td>
<td>7.99%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rap</td>
<td>10.5%</td>
<td></td>
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<td></td>
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<td>Rewp</td>
<td>6.13%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>1.71</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table II. Refined structural parameters for Nd2Zr2O7 from room-temperature single-crystal XRD data. Atomic positions for the Fd3m (origin choice 2) cubic structure are Nd, 16d(1/2, 1/2, 1/2); Zr, 16c(0,0,0); O, 48f(x, 1/2, 1/2); and O′, 8b(1/8, 1/8, 1/8). Atomic displacement parameters in units (10⁻³ Å²).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Uiso/Ueq</th>
<th>U11</th>
<th>U22 = U33</th>
<th>U12 = U13</th>
<th>U23</th>
</tr>
</thead>
<tbody>
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<td>Nd</td>
<td>5.61(15)</td>
<td>5.61(15)</td>
<td>5.61(15)</td>
<td>-1.72(3)</td>
<td>-1.72(3)</td>
</tr>
<tr>
<td>Zr</td>
<td>6.4(2)</td>
<td>6.4(2)</td>
<td>6.4(2)</td>
<td>2.50(6)</td>
<td>2.50(6)</td>
</tr>
<tr>
<td>O</td>
<td>11.6(4)</td>
<td>15.5(10)</td>
<td>9.7(5)</td>
<td>0</td>
<td>2.4(8)</td>
</tr>
<tr>
<td>O′</td>
<td>8.5(7)</td>
<td>8.5(7)</td>
<td>8.5(7)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The agreement factor for the refined value of the 48f site occupancy is, R = 2.32%, and no internal site disorder was detected in our Nd2Zr2O7 crystals. The best model for the refinement of the occupancies of the anion sites was found to be one in which only the O 48f site occupancy varies. Anisotropic thermal displacement parameters were used to refine the crystal structure. The structural parameters obtained from the best fit of the x-ray diffraction data at room temperature are listed in Table II.

The powder x-ray diffraction data measurements are sensitive to any preferred orientation present in the sample, and this is reflected in changes in the relative intensities of some of the Bragg peaks.

The powder x-ray diffraction data measurements are sensitive to any preferred orientation present in the sample, and this is reflected in changes in the relative intensities of some of the Bragg peaks.
parameters obtained using the neutron diffraction data were found to be consistent with those calculated using XRD data.

The value of $x = 0.3360(3)$ for the O atom in the 48f site confirms that both the polyhedra formed around the A (Nd) and B (Zr) sites are distorted from the ideal geometries (a perfect cube and a perfect octahedron, respectively) [37]. This fact is strongly reflected in the uniaxial nature of the A-site symmetry and in the magnetic properties of the system. The scalenohedron NdO$_8$ is formed by two short bonds Nd–O of 2.298 8(2) Å length and six bonds Nd–O of 2.561(2) Å, while the trigonal antiprism ZrO$_6$ has all six bonds Zr–O of 2.087(1) Å. The two short bonds Nd–O from the scalenohedron NdO$_8$ are stacked along the [111] direction, and the other six long bonds (Nd–O) connect the Nd ion at the center with oxygen (O) ions at the apexes of the trigonal antiprism strongly compressed along the [111] axis.

The structural features of the Nd$_2$Zr$_2$O$_7$ crystals are very similar to those of the neighboring praseodymium zirconate Pr$_2$Zr$_2$O$_7$. Rietveld refinement of the neutron diffraction data collected at the SXD beam line on a Pr$_2$Zr$_2$O$_7$ single crystal indicates a value of $x = 0.3349(1)$ for the O atom in the 48f site [41]. The oxygen polyhedra formed around the Pr and the Zr ions show a similar degree of distortion to those of neodymium zirconate. The bond lengths inside the two coordination polyhedra are as follows: 2.308 8(2) Å for the Pr–O’ bonds, 2.578(1) Å for Pr–Oa bonds, and 2.091 7(8) Å for the Zr–O bonds. Given the similarities between the structural parameters of the Nd$_2$Zr$_2$O$_7$ and Pr$_2$Zr$_2$O$_7$ pyrochlores, we can expect some similarities between the crystal fields in these two systems.

In summary, Rietveld refinements of the powder and single-crystal x-ray diffraction and neutron diffraction data confirm that Nd$_2$Zr$_2$O$_7$ adopts the cubic $Fd\bar{3}m$ pyrochlore structure. The results show no measurable cationic or anionic deficiencies of the as-grown crystals of Nd$_2$Zr$_2$O$_7$ and confirm the good quality of the boules and their suitability for future investigations, including those using neutrons as a probe, given the large size of the crystal boules grown by the floating-zone technique.

C. Magnetization and heat capacity

Field-cooled (FC) and zero-field-cooled (ZFC) magnetization versus temperature curves were measured on a Nd$_2$Zr$_2$O$_7$ single crystal aligned along three different crystallographic directions ([100], [110], and [111]). The temperature dependence of the dc magnetic susceptibility $\chi (T)$ and reciprocal dc magnetic susceptibility $\chi^{-1} (T)$ are shown in Fig. 2. No anomalies in $\chi (T)$ are observed down to 0.5 K, suggesting the absence of a magnetic transition. The magnetic susceptibility data measured along the different directions all exhibit a monotonic decrease when warming from 0.5 to 350 K, and at temperatures above 5 K the magnetic susceptibilities collected in 1 kOe along the three high-symmetry directions all overlap to within experimental error.

Attempts to fit the temperature-dependent reciprocal magnetic susceptibilities reveal that the $\chi^{-1} (T)$ data do not obey a Curie-Weiss law in the temperature range 0.5–350 K. Nevertheless, we have made fits to a Curie-Weiss law over a reduced temperature range (1.8–10 K) [see Fig. 2(b) inset], and the results of these fits have shown that for $T < 10$ K Nd$_2$Zr$_2$O$_7$ has an effective moment of $\mu_{\text{eff}} = 2.543(2) \mu_B$ ( $\mu_B$ is the Bohr magneton) and a Weiss temperature of $\theta_W = +0.200(8)$ K. Over an extended temperature range from 1.8 to 60 K, the

![FIG. 2. (Color online) (a) Temperature dependence of the dc magnetic susceptibility, $\chi$ versus $T$, in the temperature range 1.8–350 K for a crystal of Nd$_2$Zr$_2$O$_7$, with a magnetic field applied along the [100] (red), [110] (black), and [111] (orange) directions. The inset shows $\chi$ versus $T$ in the temperature range 0.5–1.75 K. (b) Measured (symbols) and calculated (the solid curve) temperature dependence of the reciprocal of the bulk dc susceptibility, $\chi^{-1}$ versus $T$, of Nd$_2$Zr$_2$O$_7$ for a field applied along the [110] direction. The temperature dependence of the reciprocal bulk dc susceptibility was calculated using the crystal field parameters determined in the present work. The inset shows $\chi^{-1}$ versus $T$ and the linear fit (using the Curie-Weiss law) to the data in the temperature range 1.8–10 K for a magnetic field applied along the [111] direction.](https://i.imgur.com/3Q5Q5Q.png)
measured temperature dependence of the dc susceptibility can be approximated by the expression \( \chi(T) = C/(T - \theta_W) + \chi_{VV} \) with the Weiss temperature of \( \theta_W = +0.150 \) K and a Van Vleck contribution of \( \chi_{VV} = 0.00346 \) emu/(mol Nd). The effective moment of \( Nd^{3+} \) in \( Nd_2Zr_2O_7 \) is smaller than the magnetic moment of \( 12/\sqrt{11} \mu_B \) of a free \( Nd^{3+} \) in the ground state \( 4I \). The value indicates a ferromagnetic coupling between the Nd spins. We have also performed magnetic susceptibility measurements on a ground piece of the \( Nd_2Zr_2O_7 \) crystal boule. The estimated Weiss temperature \( \theta_W \) was, in this case, found to be \( +0.108(6) \) K. Previous studies also reported small absolute values for the Weiss temperature in Nd-based pyrochlores, with \( \theta_W = +0.06 \) K in \( Nd_2Zr_2O_7 \) [20], \( \theta_W = -0.069(4) \) K in \( Nd_2Pb_2O_7 \) [42], and \( \theta_W = -0.31 \) K in \( Nd_2Sn_2O_7 \) [43,44]. Small differences in the absolute values obtained for \( Nd_2Zr_2O_7 \) may be explained by the fact that some measurements were carried out on aligned crystal, along well-defined crystallographic axes, while others were for polycrystalline samples. The results also appear to depend on the exact temperature range over which the fits are performed. The difference between the data collected for different directions of the applied field at low temperatures (see inset in Fig. 2(a)) cannot be explained by the contribution of the demagnetizing field; the difference in the susceptibilities corrected for the demagnetizing factor has been found to be close to 1% for all the crystallographic directions. However, this difference, which is found in a small but finite magnetic field of 1 kOe and which increases with decreasing temperature, may signal the onset of a phase transition at lower temperature. Different signs of \( \theta_W \) in compounds with different B-site cations (a chemical pressure effect) may be caused by closely competing exchange and dipolar interactions between the \( Nd^{3+} \) ions.

Figure 3 shows the magnetization as a function of applied magnetic field \( M(H) \) at a temperature of \( T = 0.5 \) K for \( Nd_2Zr_2O_7 \) along three high-symmetry directions, [100], [110], and [111]. The magnetization response is reversible with no hysteresis between the field increasing and field decreasing directions.

![FIG. 3. (Color online) Isothermal magnetization (M) as a function of applied magnetic field (H) along the [100] (red), [110] (black), and [111] (orange) directions at T = 0.5 K for a single-crystal of Nd_2Zr_2O_7.](image)

**M(H) Curves.** The data reveal a nonlinear variation of the magnetization as a function of applied field. The magnetization is highest in strong magnetic fields applied along the [100] direction and lowest for the [110] direction. The field dependence of the magnetization along the three high-symmetry directions, measured at various temperatures (see Fig. 4), indicate that the magnetic anisotropy evolves on cooling. The results of the magnetization measurements suggest that the magnetization follows a local Ising behavior, with a different dependence of \( M(H) \) along different crystallographic directions. This kind of magnetic anisotropy represents a key feature of the spin ice system, as observed in the Dy_2Ti_2O_7 and Ho_2Ti_2O_7 pyrochlore oxides [45,46]. However, the field-dependent magnetization data reveal that the magnetic anisotropy observed for the \( Nd_2Zr_2O_7 \) pyrochlore is only partially consistent with the spin ice model, as the values of the magnetic moments measured for the [100], [110], and [111] directions at the maximum applied field do not agree exactly with the ratios of the expected saturated moments for a classic spin ice configuration [45].

![FIG. 4. (Color online) Measured (symbols) and calculated (solid lines) external magnetic field dependence of the magnetization (M) of Nd_2Zr_2O_7 at various temperatures. The field was applied along the [100] (red), [110] (black), and [111] (orange) axes of the Nd_2Zr_2O_7 crystal lattice, at temperatures of (a) 1.8 K, (b) 5 K, (c) 10 K, and (d) 20 K. The field dependence of the magnetization was calculated using the crystal field parameters determined in the present work. The dashed lines in (a) indicate the theoretically expected values of the saturated magnetization satisfying the ratios \( \sqrt{2}/\sqrt{37}/2:1 \) for the [100], [111], and [110] directions, respectively, in a classical spin ice configuration [45].](image)
results for Nd$_2$Zr$_2$O$_7$ [20,47]. A continuous decrease in the specific heat with decreasing temperature is followed by an upturn at temperatures below ~7 K. Previous heat capacity studies performed on a polycrystalline sample of Nd$_2$Zr$_2$O$_7$ show a phase transition centered at 0.37 K and evidence of some magnetic ordering [20].

D. Crystal field parameters

To analyze the magnetic behavior of Nd$_2$Zr$_2$O$_7$, we consider the following Hamiltonian of a single Nd$^{3+}$ ion in an applied magnetic field $H$:

$$h = h_{\text{FI}} + h_{\text{CF}} + h_Z.$$  \hspace{1cm} (1)

Here $h_{\text{FI}}$ is a free ion standard Hamiltonian [48] that operates in the total space of 364 states of the electronic $4f^3$ configuration. The next term in (1),

$$h_{\text{CF}} = B_0^6C_2^0 + B_0^6C_4^0 + B_0^3(C_3^0 - C_3^{-1}) + B_0^6C_0^6 + B_0^3(C_3^0 - C_3^{-1}) + B_0^6(C_0^6 + C_0^6),$$ \hspace{1cm} (2)

where $h_{\text{CF}}$ is the energy of 4$f$ electrons in the crystal field of the perfect lattice with the $D_{3d}$ symmetry at the Nd$^{3+}$ sites written in the local system of coordinates with the $z$ axis along the trigonal symmetry axis. $B_0^6$ are CF parameters and $C_0^6$ are spherical tensor operators. The third term in (1) is

$$h_Z = -\mu \cdot H_{\text{loc}},$$ \hspace{1cm} (3)

where $h_Z$ is the electronic Zeeman energy. $\mu = -\mu_B(kL + 2S)$ is the magnetic moment of a Nd$^{3+}$ ion. ($L$ and $S$ are the electronic orbital and spin moments, respectively, and $k$ is the orbital reduction factor [49]). The local magnetic field affecting the Nd$^{3+}$ ions, $H_{\text{loc}} = H + H_{\text{exch}} + H_{\text{dip}} - H_D$, involves the external field $H$, the exchange and dipolar fields $H_{\text{exch}}$ and $H_{\text{dip}}$, respectively, corresponding to anisotropic exchange and magnetic dipolar interactions between the Nd$^{3+}$ ions that are considered in the self-consistent field approximation, and the demagnetizing field $H_D = 4\pi NM/3$, where $N$ is the demagnetizing factor, $M = \sum m_n/\nu$ is the magnetization, and $\nu = a^3/4$ is the unit cell volume. There are four magnetically nonequivalent rare-earth ions in the unit cell and $m_n$ is the average magnetic moment of a Nd$^{3+}$ ion belonging to the sublattice $n$.

The dipolar fields at sites $n$, $H_{\text{dip},n} = \sum_{n'\rho} Q_{n'\rho} m_{n'\rho}$ ($\rho = 4\pi/(3\nu)$), are determined by dimensionless lattice sums $Q_{n'\rho}$ which have been computed in Ref. [49]. The exchange interaction is assumed to be nonzero for the nearest-neighbor Nd$^{3+}$ ions only. In particular, the exchange interaction between the ions with radius vectors $r_1 = (1/2,1/2,1/2)$ and $r_2 = (-1/2, -1/2, -1/2)$ is approximated by [49]

$$h_{\text{exch}}(1,2) = -\lambda_1\mu_{1x}\mu_{2x} - \lambda_1\mu_{1y}\mu_{2y} - \lambda_2\mu_{1}\mu_{2},$$ \hspace{1cm} (4)

where $\mu_{1x}$, $\mu_{1y}$, and $\mu_{1z}$ are operators of the magnetic moment components along the vectors $X' = r_1 - r_2$, $Y' = r_2 \times r_1$, and $Z = r_1 + r_2$. To reduce the number of unknown parameters, we neglect in (4) an additional antisymmetric term $\lambda_{\text{DM}} Y' \cdot (\mu_1 \times \mu_2)$ (Dzyaloshinskii-Moriya like), which is allowed by symmetry of the pyrochlore lattice [50]. The values of the exchange coupling constants $\lambda_1$, $\lambda_{1\perp}$, and $\lambda_{2\perp}$, six CF parameters, and the orbital reduction factor were obtained from the fitting procedure by comparing the measured and computed magnetic field dependence of the heat capacity, the bulk dc susceptibility with temperature, and the magnetic field dependence of the isothermal magnetization.

Table IV. Crystal field parameters $B_0^6$ (cm$^{-1}$) in some Nd- and Pr-based pyrochlores. The initial CF parameters for Nd$_2$Zr$_2$O$_7$, calculated using the exchange charge model [52,53] with the parameters of the crystal lattice determined in the present work, are given in column A. The final values of the CF parameters used to simulate the dc susceptibility and the magnetization data are given in column B (see text for details).

<table>
<thead>
<tr>
<th>Nd$_2$Sn$_2$O$_7$</th>
<th>Pr$_2$Zr$_2$O$_7$</th>
<th>Pr$_2$Ir$_2$O$_7$</th>
<th>Nd$_2$Zr$_2$O$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$</td>
<td>$q$</td>
<td>Ref. [57]</td>
<td>Ref. [24]</td>
</tr>
<tr>
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<td>711</td>
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Figure 5. (Color online) Heat capacity as a function of temperature in zero applied magnetic field for a Nd$_2$Zr$_2$O$_7$ single crystal. The inset shows the temperature dependence of the heat capacity data on a logarithmic scale.
CF excitations in the Nd subsystem. This contribution as a function of temperature was estimated from the difference between the measured heat capacities of Nd2Zr2O7 and nonmagnetic La2Zr2O7 given in Ref. [54]. The results of calculations of the heat capacity of the Nd subsystem \( C_{\text{Nd}} = N_A(h^2 - (h)^2)/k_B T^2 \) (\( N_A \) is the Avogadro number, \( k_B \) is the Boltzmann constant) match well the experimental data for temperatures below 300 K (see Fig. 6). More detailed analysis, in particular, taking into account changes of phonon frequencies [55], is necessary to clarify the behavior of the relatively small differences between the heat capacities of neodymium and lanthanum zirconates at higher temperatures.

The final values of the CF parameters which were used in our simulations of the dc susceptibility and the magnetization for different directions of the external magnetic fields are presented in Table IV, column B. These parameters agree qualitatively with those found in Ref. [57] from the analysis of the CF excitations in the Pr3 ions in Pr2Sn2O7 but differ markedly from the results of the studies of the crystal fields in Nd2Ir2O7 [58] (as far as we know, this is the only earlier published set of CF parameters for Nd3+ ions in Nd-based pyrochlores) and Pr2Zr2O7 [24] (see Table IV). The CF interaction has been treated in Refs. [24] and [58] as a perturbation within the ground \( J \)-multiplet only. However, the CF splittings of the ground multiplets \( ^4I_{9/2} \) of Nd3+ and \( ^3H_4 \) of Pr3+ ions in the pyrochlores are rather large and comparable to the excitation energies of the nearest multiplets \( ^4I_{11/2} \) and \( ^3H_5 \), respectively. As a result, the \( J \) mixing should be taken into account.

The calculated energies of the sublevels of the \( ^4I_{9/2} \) ground multiplet are 0 (\( \Gamma_{56} \)), 178.5 (\( \Gamma_5 \)), 252 (\( \Gamma_6 \)), 262 (\( \Gamma_4 \)), and 785 (\( \Gamma_4 \)) (in cm\(^{-1}\)). The corresponding irreducible representations of the \( D_{5d} \) point symmetry group are presented in brackets. A transverse \( g \) factor of the Kramers doublet with the \( \Gamma_{56} \) symmetry (of dipolar-occtupolar type according to the classification proposed in Ref. [59]) is exactly zero, and our results are in line with the Ising-type magnetic anisotropy of the Nd3+ ions in compounds with the pyrochlore structure noted previously in Ref. [60]. The calculated longitudinal \( g \) factor of the ground state, \( g|| = 4.793 \), is close to the value 4.6 that has been determined in Ref. [61] for the Nd3+ ions in Nd2Mo2O7.

The temperature dependence of the dc susceptibility was calculated using the corresponding expression presented in Ref. [49], the results of the calculations are shown in Fig. 2(b). In order to match the experimental data, the orbital reduction factor \( k = 0.957 \) \( 5 \) and the exchange constants \( \lambda_{\parallel} = 0.2 \), \( \lambda_{\perp} = -0.1 \), and \( \lambda_{\perp} = 0 \) (in units of kOe/\( \mu_B \)) were introduced.

The calculated Van Vleck susceptibility of the Nd3+ ions in the ground state, averaged over four magnetically nonequivalent sites in the pyrochlore lattice, \( \chi_{VV} = 2 \sum_{j,\alpha=x,y,z} |\langle j | \mu_\alpha | g \rangle|^2/(3(E_j - E_g)) \) [here \( E_j \) and \( E_g \) are the energies of the excited states \( j \) and the ground state \( g \)], \( \chi_{VV} = 0.0032 \) emu/(mol Nd), matches very well with the value obtained from the analysis of the experimental data. (See Fig. 2 and Sec. III C above.)

Because a gap of 250 K between the ground and the first excited doublets in the energy spectrum of Nd3+ ions is rather large, the low-temperature magnetic properties of the Nd subsystem in Nd2Zr2O7 can be considered using the truncated Hilbert space spanned by the wave functions of the ground doublets only. The projection of the exchange and magnetic dipolar interactions between the nearest-neighbor Nd3+ ions on this space can be written in terms of the pseudospin \( S = 1/2 \) operators defined in local Cartesian coordinates with the \( z \) axes along the corresponding trigonal symmetry axes crossing at the angle of arccos(-1/3):

\[
H_s = (J_{\text{exch}} + J_{\text{dd}}) S_z \bar{S}_z,
\]

where \( J_{\text{exch}} = g_s^2 \mu_B^2/(2\lambda_{\parallel} - \lambda_{\perp})/3 \) and \( J_{\text{dd}} = 5g_s^2 \mu_B^2/(3|\mathbf{r}_1 - \mathbf{r}_2|^3) \). Using the values of parameters given above, we obtain \( J_{\text{exch}} = 0.257 \) K and \( J_{\text{dd}} = 0.442 \) K. So, both the exchange and dipolar interactions between the nearest-neighbor ions have antiferromagnetic character, and the exchange contribution is about half the dipolar contribution. At first glance this result contradicts with the sign of the Weiss temperature indicating a ferromagnetic coupling. However, in case of Ising-type magnetic anisotropy along the crystal ternary axes in the pyrochlore structure, the sum of antiferromagnetic interactions between a fixed rare-earth ion and the six nearest-neighbor ions leads to formation of a local magnetic field parallel to the applied field and, correspondingly, to a positive Weiss temperature [49]. A crude estimate, taking into account only the ground doublet of the Nd3+ ions and neglecting the Van Vleck contribution to the susceptibility, gives a value \( \theta_W = (g_s^2 \mu_B^2/6k_B)(2\lambda_{\parallel} - \lambda_{\perp}) + 7.52(4\pi/3)v_0 = 0.38 \) K with the dominant contribution (0.25 K) from the dipolar interactions represented by the last term in the square brackets. According to a general form of the exchange interaction [62], it may contain terms (neglected in the present work) constructed from single-ion operators \( \sum_f C_2^f(s_a s_b) \), \( \sum_f C_3^f(s_a s_b s_c) \), \( \sum_f C_4^f(s_a s_b s_c s_d) \) (the summation over \( f \) is over individual \( 4f \) electrons with spin \( s \) (on the Nd3+ ion) which mix eigenfunctions of the pseudospin \( S_z \) operator [59] and bring about fluctuations of the Ising-type magnetic moments. The effects of these
terms on the low-temperature magnetic properties of the Nd$^{3+}$ ions remain to be explored. It should also be noted that at temperatures below 1.5 K, the single-site self-consistent approximation appears not to be valid. (In particular, in contrast to the experimental data which demonstrate $\chi(T)$ doubles in the temperature range from 1 to 0.5 K, the calculated value of $\chi(T)$ increases more rapidly as the temperature decreases below 1 K.)

The simulated magnetic field dependence of the magnetization of Nd$_2$Zr$_2$O$_7$ with the magnetic field directed along the [100], [110], and [111] symmetry axes of the pyrochlore lattice at different temperatures are compared with the experimental data in Fig. 4. As can be seen from Fig. 4, the calculated field dependencies of the magnetization agree well with the experimental data.

IV. SUMMARY

We have investigated the structural properties of single crystals of the pyrochlore oxide, Nd$_2$Zr$_2$O$_7$. Powder x-ray diffraction studies of the crystal boule confirm that the $Fd\overline{3}m$ pyrochlore phase is formed, and single-crystal XRD and neutron diffraction data show a Nd$_2$Zr$_2$O$_7$ structure with no cationic or anionic deficiencies. Supplementary investigations, such as detailed inelastic neutron-scattering experiments, are now being carried out on these Nd$_2$Zr$_2$O$_7$ crystals.

The magnetic susceptibility data collected reveal a spin ice-type magnetic anisotropy and an effective ferromagnetic coupling between the Nd spins. The heat capacity decreases monotonically with decreasing temperature, followed by an upturn at low temperature. However, no sign of long-range magnetic ordering was observed in either the heat capacity or the magnetization data down to 0.5 K.

The measured temperature dependence of the magnetic susceptibility and the field dependencies of the isothermal magnetization are reproduced satisfactorily by the CF calculations and subsequent modeling in the framework of the mean-field approximation, taking into account the dipolar and the anisotropic exchange interactions between the Nd$^{3+}$ ions. The sets of CF parameters and exchange coupling constants obtained may serve as a basis for future studies of the spectral and magnetic properties of Nd-based pyrochlore magnets at low temperatures.

ACKNOWLEDGMENTS

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[14] The research community has also recently shown an increased interest in the lanthanide zirconates, $A_2Zr_2O_7$, due to their potential use in the immobilization of radioactive waste and in thermal barrier coatings.