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# Spin orders and lattice distortions of geometrically frustrated 6H-perovskites $\text{Ba}_3B'\text{Ru}_2\text{O}_9$ ( $B' = \text{La}^{3+}$ , $\text{Nd}^{3+}$ , and $\text{Y}^{3+}$ )

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The magnetic and crystal structures of the title materials have been investigated using high-resolution neutron and synchrotron x-ray powder diffraction. Ferromagnetic Ru dimers are observed in the spin-ordered ground states of all three materials, evidencing an intradimer double exchange interaction. Antiferromagnetic order between dimers breaks the degeneracy of the triangular lattice but no distortion of the  $B' = \text{La}$  and  $\text{Y}$  structures is observed. The magnetic ordering transition temperature increases with the radius of the  $B'$  cation. An anomalous 120 K structural transition in  $\text{Ba}_3\text{NdRu}_2\text{O}_9$  is attributed to Jahn-Teller distortion, evidenced by large-amplitude  $\Gamma_6$  deformations of the  $\text{NdO}_6$  octahedra. Further lattice anomalies accompany magnetic ordering transitions at 24 and 18 K in  $\text{Ba}_3\text{NdRu}_2\text{O}_9$ . Nd spins order ferromagnetically and a substantial magnetic anisotropy leads to large coercivity and  $\frac{1}{3}$ -magnetization steps in the magnetic hysteresis loop.

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## I. INTRODUCTION

The 6H-perovskites,  $\text{Ba}_3B'\text{Ru}_2\text{O}_9$ , have recently been identified as geometrically frustrated systems,<sup>1</sup> and are potentially suitable materials for observing spin liquid-type behavior,<sup>2</sup> as they contain two-dimensional triangular layers of  $\text{Ru}_2\text{O}_9$  face-sharing octahedral dimers.<sup>3</sup> Most derivatives adopt the aristotype 6H structure (with hexagonal space group  $P6_3/mmc$ ) as shown in Fig. 1, but those with  $B' = \text{Sr}$  (Ref. 4) and  $\text{Cu}$  (Ref. 5) have lower symmetry at ambient conditions.  $B'$  cations with odd charge values result in semivalent Ru states so that charge- and spin-ordered ground states may be formed. Charge ordering as  $(\text{Ru}^{5+})_2\text{O}_9$  and  $(\text{Ru}^{6+})_2\text{O}_9$  dimers has recently been reported for  $\text{Ba}_3\text{NaRu}_2\text{O}_9$  accompanied by the opening of a spin gap and a structural phase transition at 210 K to monoclinic  $P2_1/c$  symmetry.<sup>6</sup> The opening of a spin gap in  $\text{Ba}_3\text{BiRu}_2\text{O}_9$  has also recently been reported,<sup>7</sup> resulting in a phase transition to  $C2/c$  symmetry at 176 K.

Magnetic ordering transitions are evident in susceptibility measurements from  $\text{Ba}_3B'\text{Ru}_2\text{O}_9$  materials, but spin arrangements have been determined by neutron diffraction only for  $B' = \text{Ni}^{2+}$  and  $\text{Co}^{2+}$ .<sup>5,8,9</sup> The  $(\text{Ru}^{5+})_2\text{O}_9$  spin dimers are antiferromagnetic and are coupled to ordered Ni or Co spins.  $B' = R^{3+}$  (rare earth) and  $\text{Y}^{3+}$  materials have Néel transitions at  $T_N < 28$  K and remain hexagonal down to 2 K,<sup>3,10</sup> except for  $B' = \text{Nd}^{3+}$  in which a transition to  $C2/c$  symmetry has been reported at 120 K in addition to two low-temperature transitions, at  $T_1 = 24$  and  $T_2 = 17$  K, observed in magnetization and heat capacity measurements.<sup>11</sup> Broad features in magnetic susceptibility and specific heat measurements at high temperatures were interpreted as evidence for local antiferromagnetic pairing within  $\text{Ru}_2\text{O}_9$  dimers.<sup>3</sup> Previous neutron powder diffraction data revealed ferromagnetic ordering of  $\text{Nd}^{3+}$  moment in  $\text{Ba}_3\text{Nd}^{3+}\text{Ru}_2\text{O}_9$  below  $T_1$ , but the nature of the further order at  $T_2$  was unclear.<sup>11</sup>  $B' = \text{Y}$  and  $\text{La}$  materials have not been investigated by neutron diffraction. Here we report low-temperature neutron diffraction studies of the spin order in  $\text{Ba}_3B'\text{Ru}_2\text{O}_9$  ( $B' = \text{La}$ ,  $\text{Nd}$ , and  $\text{Y}$ ) which show that the spin dimers are ferromagnetic in all the materials, with

no charge order apparent. In the case of  $B' = \text{Nd}^{3+}$  we find an antiferromagnetic order of the ferromagnetic Ru dimers and canting of Nd moments below  $T_2$ . We also evidence local distortions around  $\text{Nd}^{3+}$  that may drive the 120 K structural transition.

## II. EXPERIMENT

Samples of  $\text{Ba}_3B'\text{Ru}_2\text{O}_9$  ( $B' = \text{La}$ ,  $\text{Y}$ ,  $\text{Nd}$ ) were prepared by calcining pellets made from stoichiometric amounts of  $\text{RuO}_2$ ,  $\text{BaCO}_3$ , and  $B'_2\text{O}_3$  at 900 °C. The pellets were heated to between 1100 °C and 1400 °C for 72 h with multiple cycles of regrinding and repelletization, following previously reported methods of preparation.<sup>3</sup> The samples were found to be phase pure by laboratory x-ray diffraction. High-resolution synchrotron x-ray powder diffraction data [wavelength = 0.399 83(4) Å] were collected from the ID31 beamline at ESRF for  $B' = \text{La}$ ,  $\text{Y}$  at room temperature and for  $B' = \text{Nd}$  in the range 10–295 K. High-resolution neutron powder diffraction data were collected for  $B' = \text{La}$  and  $\text{Y}$  at the time-of-flight diffractometer HRPD at ISIS from 10 and 2 K, respectively, up to 300 K. Neutron powder diffraction data from all three samples were also measured down to 1.6 K at the time-of-flight neutron powder diffractometer WISH at ISIS up to a  $d$  spacing of 30 Å.<sup>12</sup> Magnetization-field hysteresis loops were collected for the  $B' = \text{Nd}$  samples at 2, 15, 20, 30, and 150 K.

## III. RESULTS

### A. $\text{Ba}_3\text{LaRu}_2\text{O}_9$ and $\text{Ba}_3\text{YRu}_2\text{O}_9$

Results from refinement of the crystal structures against the ID31 data at 300 K are summarized in Table I, and are consistent with previously published structural models.<sup>3</sup> Additional peaks due to magnetic scattering were observed in the neutron powder diffraction profiles for  $B' = \text{La}$  and  $\text{Y}$  samples (Fig. 2) below their respective magnetic transition temperatures of 22 and 4.5 K, previously reported from susceptibility and heat capacity measurements.<sup>10</sup> The

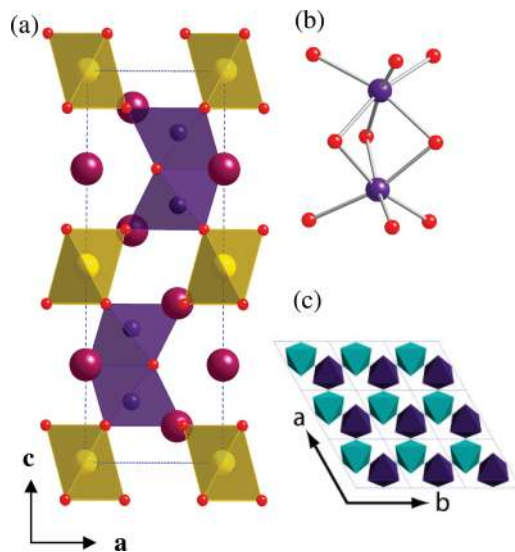


FIG. 1. (Color online) Crystal structure of 6H  $Ba_3B'Ru_2O_9$  hexagonal perovskites: (a) projection on the  $ac$  plane; (b) a  $Ru_2O_9$  dimer; (c) the triangular lattice of  $Ru_2O_9$  dimers with light/dark shading of dimers centered in the  $z = \frac{1}{4}/z = \frac{3}{4}$  planes.

magnetic peaks for both materials are indexed by the  $(0 \frac{1}{2} 0)$  propagation vector, equivalent to an orthorhombic  $a_o = a$ ,  $b_o = \sqrt{3}a$ ,  $c_o = c$   $Cmcm$  superstructure of the hexagonal  $P6_3/mmc$  cell. The irreducible representations and basis vectors of the Ru spins in  $P6_3/mmc$  under the propagation vector  $(0 \frac{1}{2} 0)$ , generated from the program BASIREPS of the FULLPROF suite,<sup>13</sup> are shown in Table II.

Models containing antiferromagnetic  $Ru_2O_9$  spin dimers, as proposed from previous magnetic heat capacity results,<sup>10</sup> did not fit the magnetic intensities of  $Ba_3LaRu_2O_9$ . However, a model [Fig. 2(b), inset] of ferromagnetic dimers described by the basis vectors from two different representations

TABLE I. Rietveld structural refinement model for  $Ba_3B'Ru_2O_9$ ,  $B' = La$  and  $Y$  at 11 and 2 K, respectively, against neutron powder diffraction data (from HRPD at ISIS). Refined hexagonal lattice parameters, fractional coordinates, isotropic thermal U factors, and fitting residual  $wR_p$  values are shown. Estimated standard deviations are in parentheses. Atomic positions in space group  $P6_3/mmc$  are Ba1  $(0,0,\frac{1}{4})$ , Ba2  $(\frac{1}{3},\frac{2}{3},z)$ ,  $B'$   $(0,0,0)$ , Ru  $(\frac{1}{3},\frac{2}{3},z)$ , O1  $(x,2x,\frac{1}{4})$ , and O2  $(x,2x,z)$ .

$B'$	La	Y
$a$ (Å)	5.9492(1)	5.86560(9)
$c$ (Å)	14.9981(4)	14.4817(2)
Ba2 $z$	0.8909(1)	0.9061(1)
Ru $z$	0.16556(8)	0.16418(7)
O1 $x$	0.4873(1)	0.4892(1)
O2 $x$	0.17889(8)	0.17663(9)
O2 $z$	0.40471(4)	0.3532(2)
Ba $U_{iso}$ (Å <sup>2</sup> )	0.0081(3)	0.0026(2)
$B'$ $U_{iso}$ (Å <sup>2</sup> )	0.0066(3)	0.0026(3)
Ru $U_{iso}$ (Å <sup>2</sup> )	0.0024(2)	0.0016(2)
O $U_{iso}$ (Å <sup>2</sup> )	0.0108(2)	0.0060(1)
$wR_p$ (%)	6.66	5.75

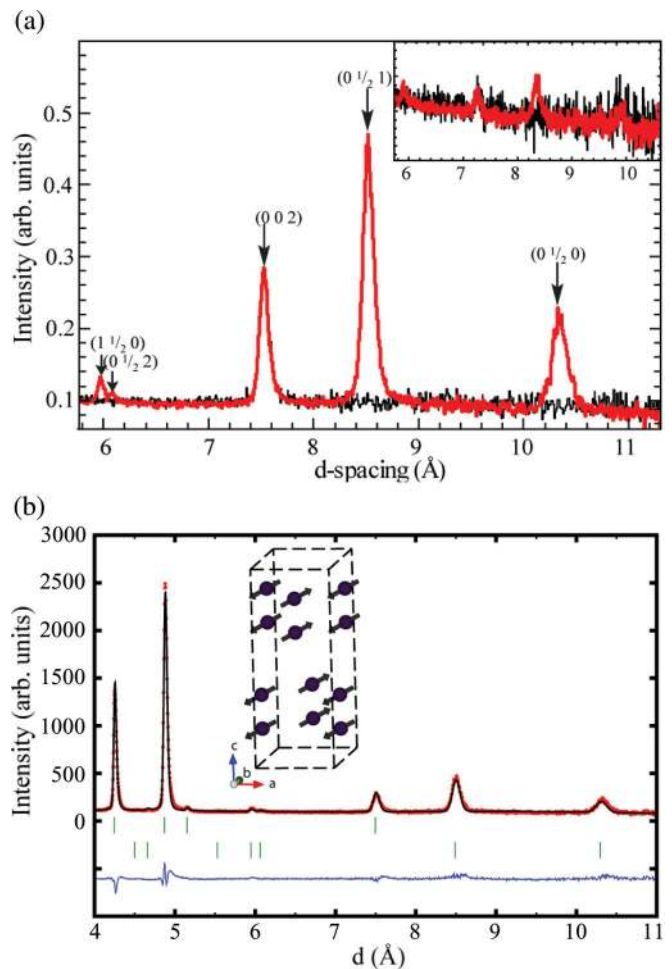


FIG. 2. (Color online) (a) Overlay of neutron diffraction spectra (from WISH at ISIS) for  $Ba_3B'Ru_2O_9$  with  $B' = La$  at 40 and 10 K (red), with magnetic peaks evident in the latter profile. The inset shows a similar comparison of profiles for the  $B' = Y$  analog at 8 and 1.6 K, where less intense magnetic intensities are observed. (b) Rietveld fit to  $B' = La$  data at 1.6 K with the magnetic intensities (lower tick marks) modeled by the  $(0 \frac{1}{2} 0)$  model shown.

accounts well for the observed magnetic diffraction intensities [Fig. 2(b)]. The  $\Psi_1(\Gamma_5)$  basis fits the  $(0 \frac{1}{2} l)$  magnetic peaks but predicts zero intensity for the  $(1 \frac{1}{2} 0)$  peak which is clearly observed in Fig. 2(a), hence the need for an additional  $\Psi_2(\Gamma_3)$  component.  $\Psi_1(\Gamma_5)$  and  $\Psi_2(\Gamma_3)$  respectively describe Ru spin components parallel to the  $a_o$  and  $c_o$  vectors of the orthorhombic supercell, with values  $m_x = 1.3(1)\mu_B$  and  $m_z = 0.6(2)\mu_B$ , and resultant moment  $1.4(2)\mu_B$ , at 1.6 K. The magnetic peaks for  $Ba_3YRu_2O_9$  at 1.6 K are less intense and the corresponding refined components are  $m_x = 0.4(3)\mu_B$  and  $m_z = 0.2(5)\mu_B$ , with a resultant moment of  $0.5(6)\mu_B$ . Although the fitting errors on these values are large, the appearance of the same magnetic reflections including a weak  $(1 \frac{1}{2} 0)$  peak [Fig. 2(a), inset] demonstrates that both magnetic bases are present for  $Ba_3YRu_2O_9$ . The moments in both materials are significantly reduced from the ideal value of  $2.5\mu_B$ , consistent with a frustrated spin order. Nearest-neighbor Ru-Ru alignments are ferromagnetic along one side and antiferromagnetic on two sides of each plaquette in the

TABLE II. Irreducible representations and basis vectors of the space group  $P6_3/mmc$  for the Ru site  $(\frac{1}{3}, \frac{2}{3}, z)$  (where  $z = 0.16556$  and  $0.16418$  for  $B' = \text{La}$  and  $\text{Y}$ , respectively) under the propagation vector  $(0 \frac{1}{2} 0)$ . The magnetic structure of  $\text{Ba}_3\text{LaRu}_2\text{O}_9$  in Fig. 2(b) is a combination of the basis vectors  $\Gamma_3(\Psi_2)$  and  $\Gamma_5(\Psi_1)$ .

Irreducible representations	Basis vectors	$x, y, z$			$-x, -y, z + \frac{1}{2}$			$x - y, -y, -z$			$-x + y, y, -z + \frac{1}{2}$		
		$m_x$	$m_y$	$m_z$	$m_x$	$m_y$	$m_z$	$m_x$	$m_y$	$m_z$	$m_x$	$m_y$	$m_z$
$\Gamma_1$	$\Psi_1$	1	0	0	-1	0	0	1	0	0	-1	0	0
$\Gamma_2$	$\Psi_1$	1	2	0	-1	-2	0	-1	-2	0	1	2	0
	$\Psi_2$	0	0	1	0	0	1	0	0	-1	0	0	-1
$\Gamma_3$	$\Psi_1$	1	2	0	-1	-2	0	1	2	0	-1	-2	0
	$\Psi_2$	0	0	1	0	0	1	0	0	1	0	0	1
$\Gamma_4$	$\Psi_1$	1	0	0	-1	0	0	-1	0	0	1	0	0
$\Gamma_5$	$\Psi_1$	1	0	0	1	0	0	1	0	0	1	0	0
$\Gamma_6$	$\Psi_1$	1	2	0	1	2	0	-1	-2	0	-1	-2	0
	$\Psi_2$	0	0	1	0	0	-1	0	0	-1	0	0	1
$\Gamma_7$	$\Psi_1$	1	2	0	1	2	0	1	2	0	1	2	0
	$\Psi_2$	0	0	1	0	0	-1	0	0	1	0	0	-1
$\Gamma_8$	$\Psi_1$	1	0	0	1	0	0	-1	0	0	-1	0	0

triangular  $ab$ -plane lattice of dimers. Breaking of degeneracy should lead to an orthorhombic distortion of the hexagonal lattice. This was tested by an orthorhombic  $Cmcm$  supercell to the low-temperature HRPD data, but no significant deviation of the  $a_0/b_0$  ratio was found, as shown in Fig. 3.

### B. $\text{Ba}_3\text{NdRu}_2\text{O}_9$

A structural transition at 120 K and two probable spin-ordering transitions, at 24 and 17 K, were previously reported in this material.<sup>11</sup> Peak splittings consistent with the reported distortion from hexagonal  $P6_3/mmc$  to monoclinic  $C2/c$  symmetry at 120 K were observed in the low-temperature

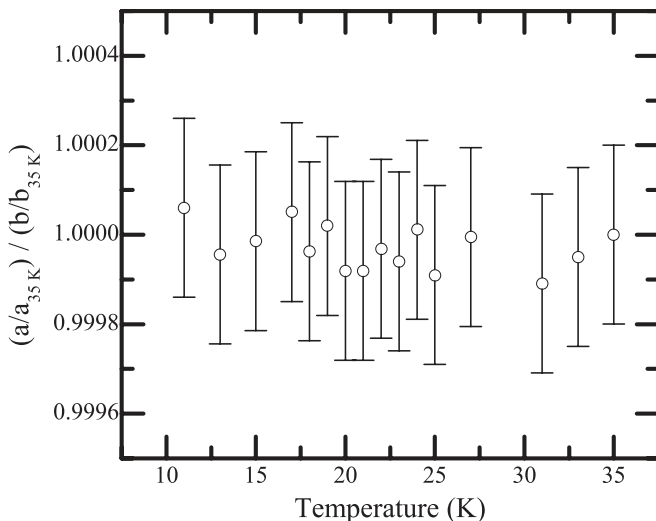


FIG. 3. Variation of the  $a/b$  lattice parameter ratio for  $\text{Ba}_3\text{LaRu}_2\text{O}_9$  from Pawley (coordinate independent) fits in orthorhombic space group  $Cmcm$  to high-resolution neutron powder diffraction data from HRPD at ISIS, normalized to the 35 K ratio. The normalized ratio does not deviate from unity on cooling through the 22 K magnetic ordering transition, showing that the lattice retains hexagonal symmetry within the resolution of the experiment.

x-ray diffraction patterns. The thermal evolution of lattice parameters extracted from Rietveld fits to the synchrotron powder diffraction data are plotted in Fig. 4(a). The angle  $\beta$  increases from  $90^\circ$  to around  $90.9^\circ$  on cooling through the transition, and the cell lengths vary monotonically down to the onset of magnetic order at 24 K. Lattice parameters in the range 1.6–30 K were extracted from the neutron powder diffraction data [Fig. 4(b)]. All four monoclinic lattice parameters have anomalies at  $T_1 = 24$  K, and a further discontinuity at  $T_2 = 18$  K is observed in the variation of the  $\beta$  angle.

To gain further insights into the structural transition in  $\text{Ba}_3\text{NdRu}_2\text{O}_9$  and the structural anomalies accompanying the magnetic transitions, we have performed distortion mode analyses of the monoclinic structure with respect to the hexagonal parent  $P6_3/mmc$  symmetry using the ISODISPLACE program<sup>14</sup> and the JEDIT interface<sup>15</sup> to the Rietveld refinement program TOPAS.<sup>16</sup> The results from fits to the synchrotron and neutron powder diffraction data are shown in Fig. 5. The distortion modes are labeled according to the site in  $P6_3/mmc$  that they act on, and the symmetry of their order parameter direction. The  $\Gamma_6$  modes are the primary order parameters for the structural phase transition as they have the largest amplitudes, and also because a  $\Gamma_6$  distortion mode alone would imply the final  $C2/c$  space group symmetry. The largest amplitude  $\Gamma_6$  modes that emerge below the 120 K structural transition [Fig. 5(a)] involve the O2 oxygen atoms which are coordinated to the  $\text{Nd}^{3+}$  ions. The O2 sites also coordinate Ru, which may account for the large amplitude of the  $\Gamma_6(\text{Ru})$  mode. Amplitudes from the neutron refinements in Fig. 5(b) show a large change in one of the  $\Gamma_4(\text{O}2)$  modes below the 25 K magnetic transition. The effects of this on the  $\text{NdO}_6$  coordination octahedron are illustrated in Fig. 6. The Nd-O bond distances do not change significantly, but order-parameter-like changes in O-Nd-O bond angles occur below the 25 K transition. Refined structural parameters for  $\text{Ba}_3\text{NdRu}_2\text{O}_9$  at 1.6 K are shown as Supplemental Material.<sup>17</sup>

Magnetic neutron diffraction peaks were observed below the previously reported  $T_1 = 25$  K and  $T_2 = 18$  K magnetic transitions.<sup>11</sup> Magnetic diffraction peaks [Fig. 7(a)] observed

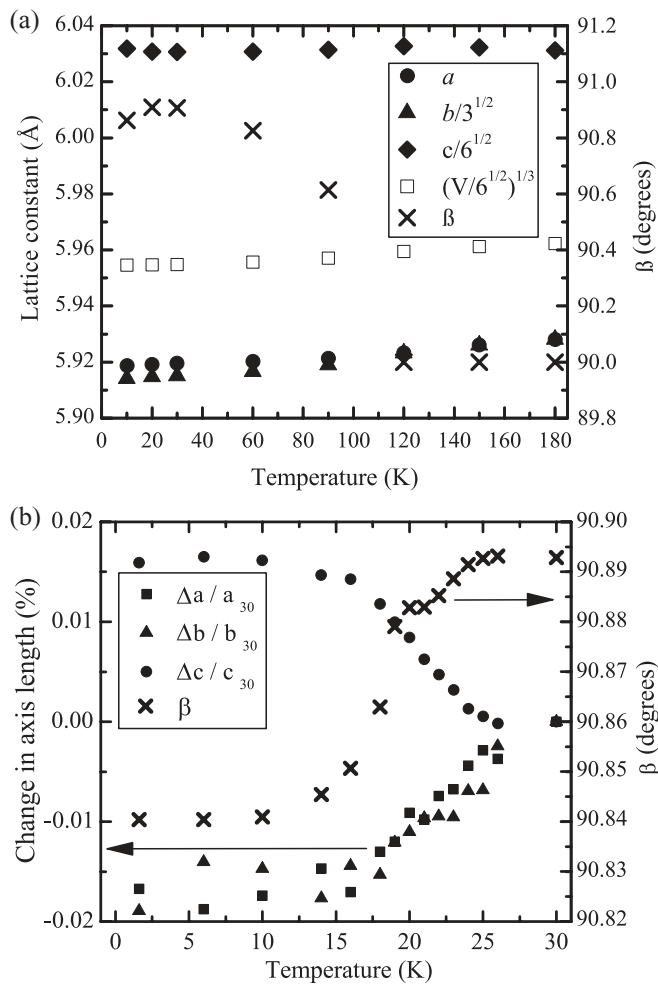


FIG. 4. Thermal evolution of lattice parameters for  $\text{Ba}_3\text{NdRu}_2\text{O}_9$ : (a) through the 120 K hexagonal to monoclinic phase transition, showing parameters from Rietveld fits to synchrotron powder x-ray diffraction data; (b) around the  $T_1 = 24$  K and  $T_2 = 18$  K magnetic transitions, using data from fits to neutron powder diffraction data, with changes in axis lengths relative to 30 K values of  $a = 5.91997(3)$ ,  $b = 10.25053(7)$ , and  $c = 14.77275(10)$  Å.

at 20 K indexed on a (000) propagation vector of the  $C2/c$  cell. They were fitted by a ferromagnetic order of  $\text{Nd}^{3+}$  moments parallel to  $c$  [Fig. 7(b)], corresponding to the  $\Psi_3(\Gamma_2)$  basis for (000) order in Table III. The refined magnitude of  $1.56(7)\mu_B$  at 20 K is consistent with the previously published result obtained from neutron powder diffraction of  $1.65(8)$  at 10 K.<sup>11</sup> No direct evidence for simultaneous ordering of Ru moments at  $T_1$  is observed, although this is known to occur in materials such as the related double perovskite  $\text{Ba}_2\text{NdRuO}_6$ .<sup>18</sup> Fits to our data show that any ferromagnetically ordered Ru component has magnitude substantially lower than  $0.4\mu_B$ .

Below  $T_2 = 18$  K, additional magnetic peaks characterized by two propagation vectors appear [Fig. 7(a)]. The (001) peak, which is systematically absent in the nuclear scattering, evidences a further, antiferromagnetic, (0 0 0) Nd spin component. This has refined magnitude  $0.5(1)\mu_B$  at 1.6 K and can be modeled by a canting of the Nd moment along the  $a$  or  $b$  directions. Canting parallel to  $b$  is considered most likely as this is described by the  $\Psi_2(\Gamma_2)$  basis vector belonging to the same

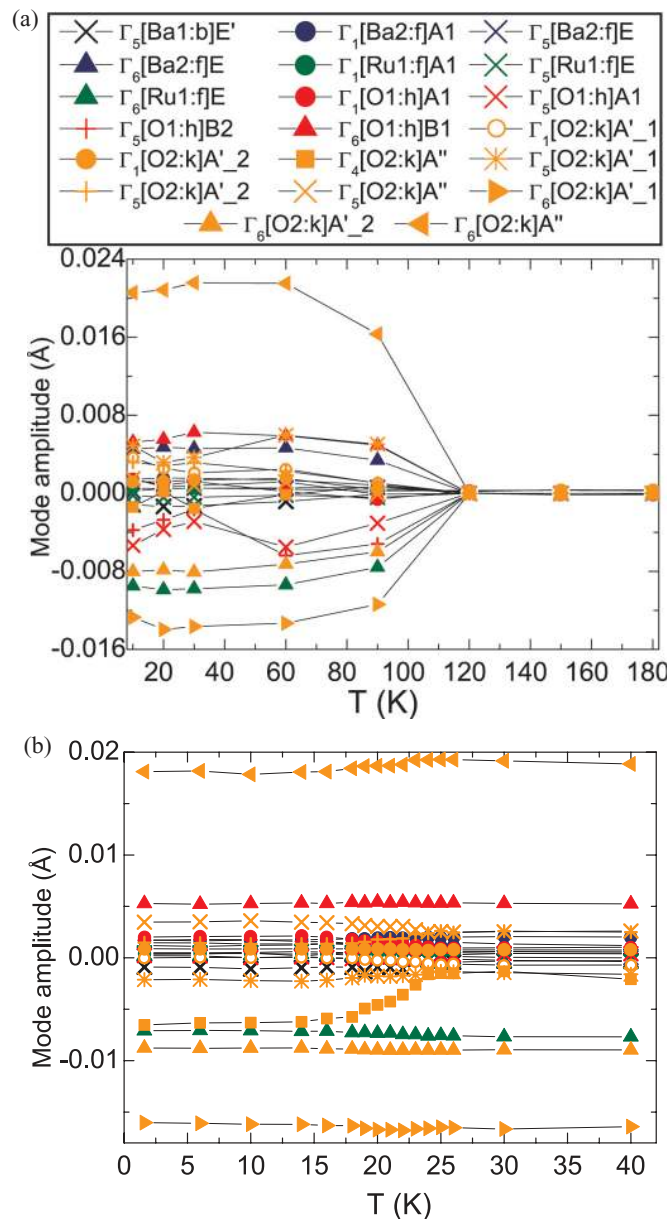


FIG. 5. (Color online) Thermal evolution of the distortion mode amplitudes for  $\text{Ba}_3\text{NdRu}_2\text{O}_9$  from the refinements shown in Fig. 4. Distortion mode labels for both plots are shown above (a).

representation as the ferromagnetic  $\Psi_3(\Gamma_2)$  Nd spin component (Table III). Several further magnetic Bragg peaks ( $\frac{1}{2} 1 2$ ), ( $\frac{1}{2} 1 1$ ), and ( $\frac{1}{2} 1 0$ ) [Fig. 7(a)] that belong to the propagation vector ( $\frac{1}{2} 0 0$ ) were also observed. Symmetry analysis of the Ru sublattice in space group  $C2/c$  under this propagation vector is summarized in Table III. The Ru site is split in this analysis, but the data available did not enable the two Ru spins to be fitted independently and only models with either a parallel or an antiparallel constraint on the moments within dimers were considered. A model of ferromagnetic Ru dimers, coupled antiferromagnetically to neighboring dimers [Fig. 7(c)], which transforms under  $\Gamma_1$  of Table III, was found to give the best fit. This is equivalent to the ordered  $\text{Ru}:m_x$  components observed in  $\text{Ba}_3\text{LaRu}_2\text{O}_9$  and  $\text{Ba}_3\text{YRu}_2\text{O}_9$  above. However, there are still some discrepancies between observed and calculated

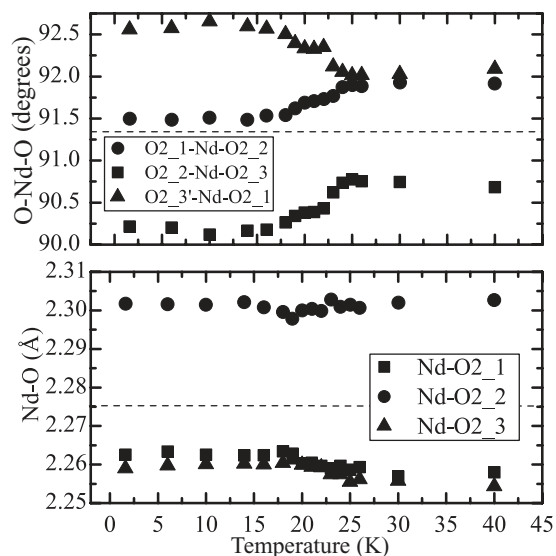


FIG. 6. Thermal evolution of the  $\text{NdO}_6$  coordination environment in the monoclinic phase of  $\text{Ba}_3\text{NdRu}_2\text{O}_9$  at low temperatures. Bond distances and angles are extracted from Rietveld fits to neutron powder diffraction data. The angles shown are equal above the 120 K structural transition, as are the distances..

magnetic intensities, and a more extensive set of magnetic diffraction data would be needed to determine the full spin-ordered structure. The temperature evolution of the three  $\text{Ba}_3\text{NdRu}_2\text{O}_9$  magnetic components is shown in Fig. 7(b). The ferromagnetic  $\text{Nd}:m_z(0\ 0\ 0)$  moment is an order parameter for the  $T_1 = 25$  K transition, and the antiferromagnetic  $\text{Nd}:m_y(0\ 0\ 0)$  and  $\text{Ru}:m_x(\frac{1}{2}\ 0\ 0)$  components have similar behavior below  $T_2 = 18$  K.

Magnetization-field loops for  $\text{Ba}_3\text{NdRu}_2\text{O}_9$  are shown in Fig. 7(d). The saturated moment of  $\sim 1.2\mu_B/\text{formula unit}$  at 2–20 K is comparable to the magnitude of the ordered ferromagnetic  $\text{Nd}:m_z(0\ 0\ 0)$  component. A simple hysteresis loop with little coercivity is observed at 15 and 20 K, but a substantial coercive field of 1.1 T is observed at 2 K. In addition,  $\frac{1}{3}$  (of maximum) -magnetization steps are observed in the 2 K loop. These evidence coherent reversal of ferromagnetic Nd chains or planes, as discussed later.

TABLE III. Irreducible representations and basis vectors of the space group  $C2/c$  for Ru at  $(x, y, z) = (0.994, 0.332, 0.836)^{11}$  under propagation vector  $(\frac{1}{2}\ 0\ 0)$ , and for Nd at  $(0, 0, 0)$  under vector  $(0\ 0\ 0)$ , in  $\text{Ba}_3\text{NdRu}_2\text{O}_9$ . Ru is split into independent sites shown as  $\text{Ru}_1$  and  $\text{Ru}_2$ .  $\Psi_3(\Gamma_2)$  and  $\Psi_2(\Gamma_2)$  respectively describe the ferromagnetic (at  $T_1$ ) and antiferromagnetic (at  $T_2$ ) orders of Nd moments under propagation vector  $(0\ 0\ 0)$ , and  $\Psi_1(\Gamma_1)$  was used for the  $(\frac{1}{2}\ 0\ 0)$  magnetic order of Ru moments at  $T_2$ .

Irreducible representations	Basis vectors	$\text{Ru}_1(x, y, z)/\text{Ru}_2(-x, y, -z + \frac{1}{2})/\text{Nd}(x, y, z)$			$\text{Ru}_2(x, -y, z + \frac{1}{2})/\text{Ru}_1(-x, -y, -z)/\text{Nd}(-x, y, -z + \frac{1}{2})$		
		$m_x$	$m_y$	$m_z$	$m_x$	$m_y$	$m_z$
$\Gamma_1$	$\Psi_1$	1	0	0	-1	0	0
	$\Psi_2$	0	1	0	0	1	0
	$\Psi_3$	0	0	1	0	0	-1
$\Gamma_2$	$\Psi_1$	1	0	0	1	0	0
	$\Psi_2$	0	1	0	0	-1	0
	$\Psi_3$	0	0	1	0	0	1

#### IV. DISCUSSION

Magnetic neutron diffraction shows that ferromagnetic Ru spin dimers are present in all of the  $\text{Ba}_3B'\text{Ru}_2\text{O}_9$  ( $B' = \text{La}, \text{Nd}, \text{Y}$ ) ground states. This is in contrast to predictions for these materials,<sup>3</sup> and to observations of antiferromagnetic dimers in  $B' = \text{Co}^{2+}$  and  $\text{Ni}^{2+}$  materials<sup>8</sup> and evidence for antiferromagnetic or spin-singlet  $(\text{Ru}^{5+})_2$  and  $(\text{Ru}^{6+})_2$  dimers in charge-ordered  $\text{Ba}_3\text{NaRu}_2\text{O}_9$ .<sup>6</sup> The key difference is that the Ru ions in the latter materials have integral charge states, whereas in the rare earth series an average  $\text{Ru}^{4.5+}$  state is apparent with no evidence for charge ordering. Ferromagnetism is favored by delocalization of the single minority (down-)spin  $t_{2g}$  electron in each dimer, so the idealized orbital populations are  $t_{2g}(\uparrow)^3 t_{2g}(\downarrow)^{0.5}$ . This is a molecular example of the double (Zener) exchange interaction observed in mixed valent manganese oxide perovskites such as  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ . The short Ru-Ru separation in the dimers ( $D_{\text{Ru-Ru}} \sim 2.5$  Å) facilitates this direct interaction between the  $t_{2g}$  orbitals.

The same antiferromagnetic order of ferromagnetic Ru dimers is observed in  $\text{Ba}_3B'^{3+}\text{Ru}_2\text{O}_9$  for  $B' = \text{Y}, \text{Nd}$ , and  $\text{La}$ , but the respective ordering temperatures of 4.5, 18, and 22 K vary markedly. This is attributed to a lattice effect controlled by the  $B'^{3+}$  cation size—such sensitivity is typical in perovskite-related oxides.<sup>19,20</sup> Figure 8 shows that the magnetic ordering temperature (reported Néel temperatures for  $B' = \text{rare earth}$  and  $\text{Y}$ ,<sup>3</sup> the value for  $\text{Bi}^{3+}$  is assigned from the magnetic heat capacity;<sup>7</sup> spin freezing transition for  $B' = \text{In}^{3+}$ )<sup>1</sup> increases smoothly with the ionic radius of  $B'$ . This variation implies that the same antiferromagnetic arrangement of ferromagnetic dimers is present throughout the series. The observed  $T_2 = 18$  K of  $\text{Ba}_3\text{NdRu}_2\text{O}_9$  follows the trend for the other  $\text{Ba}_3B'^{3+}\text{Ru}_2\text{O}_9$  materials in Fig. 8, showing that the lattice distortion and ordering of Nd moments at higher temperatures appear not to perturb the Ru spin order.

Although the observed long-range spin order breaks the triangular degeneracy of the lattice, no evidence for an orthorhombic distortion of the hexagonal lattice is evident in  $\text{Ba}_3\text{LaRu}_2\text{O}_9$  (Fig. 3), which has the highest  $T_N$  of the  $B' = \text{rare earth}$  series. Hence, the increase in  $T_N$  with  $B'$  size does not result from relief of magnetic frustration, and is probably related to geometric enhancement of superexchange interactions between dimers.

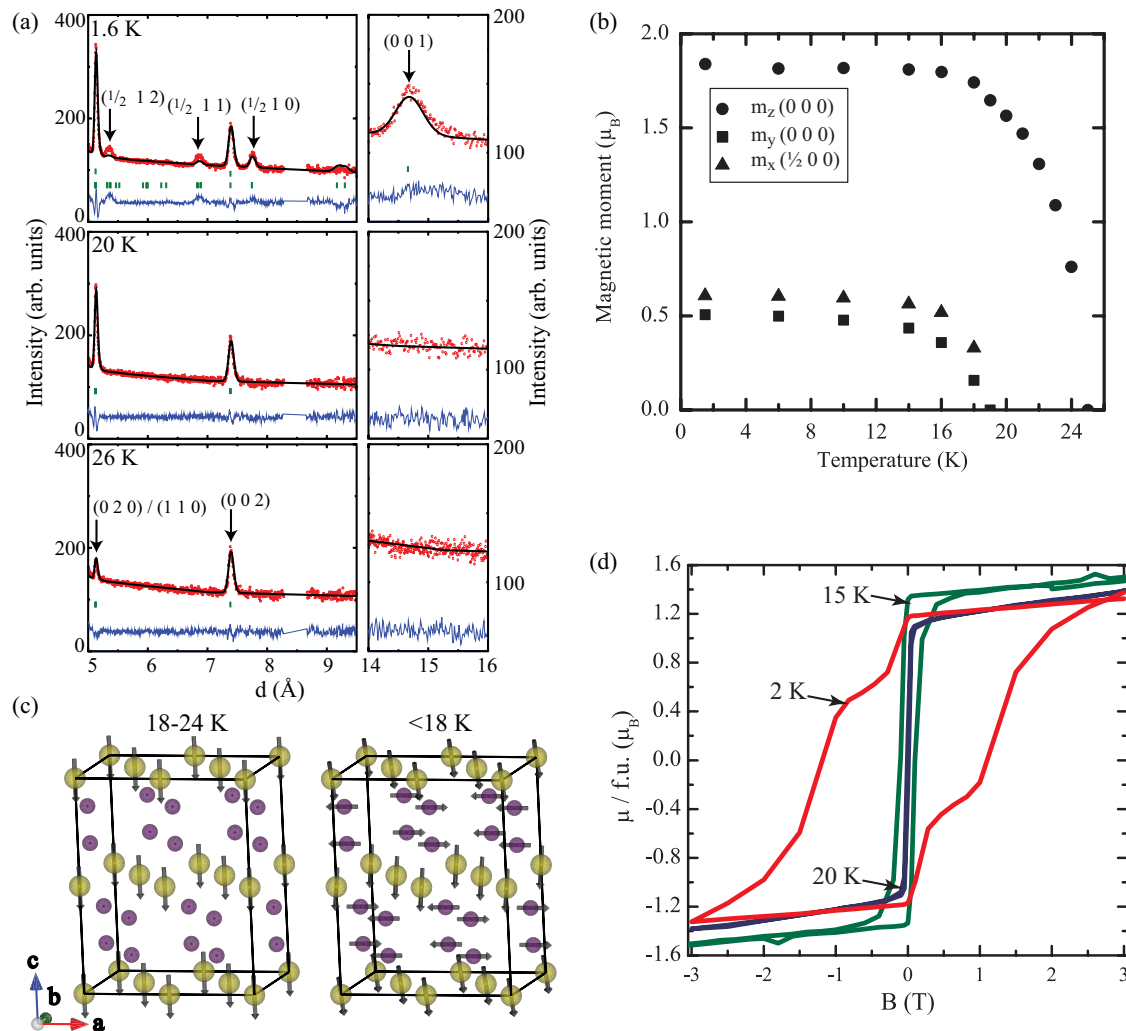


FIG. 7. (Color online) Magnetic ordering results for  $\text{Ba}_3\text{NdRu}_2\text{O}_9$ . (a) Fits to regions of the neutron diffraction data from  $2\theta = 58^\circ$  (left) and  $27^\circ$  (right) detector banks of WISH at ISIS. Ferromagnetic order of Nd moments at  $T_1 = 24$  K is evidenced by the enhancement of  $(110)$  intensity on cooling from 26 to 20 K.  $(\frac{1}{2} 1 l)$  peaks from Ru spin order and  $(001)$  from Nd spin canting emerge on cooling through  $T_2 = 18$  K. (b) Thermal evolution of Nd  $\Psi_3(\Gamma_2)$   $m_z(0 0 0)$  and  $\Psi_2(\Gamma_2)$   $m_y(0 0 0)$ , and Ru  $\Psi_1(\Gamma_1)$   $m_x(0 0 \frac{1}{2})$  spin components. (c) Magnetic structures between  $T_1$  and  $T_2$  (left) and below  $T_2$ , showing Nd/Ru as large/small atoms. (d) Magnetic hysteresis loops at 2, 15, and 20 K, showing  $\frac{1}{3}$ -magnetization steps at 2 K.

$\text{Ba}_3\text{NdRu}_2\text{O}_9$  is remarkable in displaying a lattice distortion at a relatively high temperature (120 K) that is not observed in any of the other  $\text{Ba}_3B'\text{Ru}_2\text{O}_9$  ( $B'^{3+} = \text{rare earth}$ ) materials.<sup>3</sup> This is clearly not a size-driven effect, as the analogs with larger  $B' = \text{La}$  and smaller  $B' = \text{Y}$  both remain hexagonal down to at least 2 K. Crystal-field effects on  $4f^n$  rare earth ion lattices are usually weak, but are the only plausible explanation for the anomalous lattice behavior of  $\text{Ba}_3\text{NdRu}_2\text{O}_9$ . The  $^4I_{9/2}$  ground state of  $4f^3$   $\text{Nd}^{3+}$  splits into five Kramers doublets, and the lowest two in energy are degenerate in an octahedral crystal field, and so this environment is sensitive to Jahn-Teller distortion. This is corroborated by our structural data in Figs. 4 and 5, which show that the largest distortion amplitudes at the 120 K transition are predominantly  $\Gamma_6$  modes associated with local deformations of the  $\text{NdO}_6$  octahedra. These break the equivalence of Nd-O distances and O-Nd-O angles (Fig. 6).

Magnetic order of the  $\text{Nd}^{3+}$  spins induces further lattice distortion through spin-orbit coupling, as evidenced by the cell parameter anomalies at the magnetic  $T_1$  and  $T_2$  transitions shown in Fig. 4(b). The distortion mode analysis in Fig. 5(b) demonstrates that a  $\Gamma_4$  distortion of the  $\text{NdO}_6$  octahedra is the main internal order parameter for the additional deformation below the  $T_1 = 24$  K onset of magnet order. This twisting deformation creates further disparity between O-Nd-O angles but does not affect the Nd-O distances.

The presence of lattice distortions and two magnetically active cations makes analysis of the spin order in  $\text{Ba}_3\text{NdRu}_2\text{O}_9$  more complex than that in the La and Y analogs, but the main features are clear from the present powder neutron study. The  $T_1 = 24$  K transition corresponds to a ferromagnetic order of only  $\text{Nd}^{3+}$  spins, parallel to the  $c$  axis. Two antiferromagnetic modes emerge at the  $T_2 = 18$  K transition. The

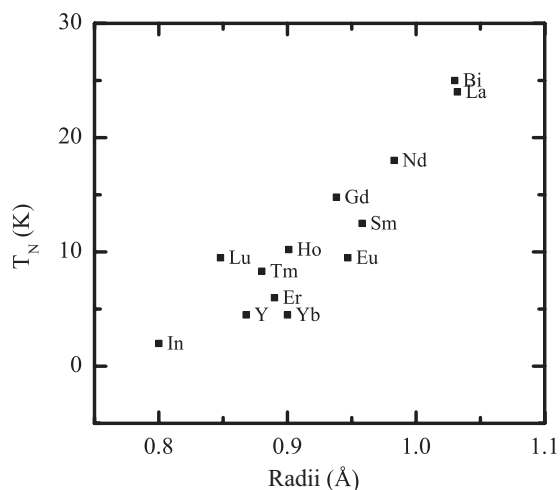


FIG. 8. Plot of the reported Ru spin-ordering temperatures of 6H-perovskites  $Ba_3B'Ru_2O_9$  against ionic radius of the trivalent  $B'$  ions.

antiferromagnetic order of Ru dimers is like that observed in  $Ba_3LaRu_2O_9$  and  $Ba_3YRu_2O_9$ , and this induces a further antiferromagnetic component to the  $Nd^{3+}$  spin order, corresponding to an overall canting of the moments. The concomitant ordering of two modes that belong to different propagation vectors implies coupling between the two propagation vectors, which would necessitate a doubling of the  $\Gamma$  point such that it contains both representations. This may account for why a complete description of the magnetic structure is not achieved within the present representational analysis. Simulated annealing of the magnetic structure in a larger supercell (containing eight Nd and 16 Ru sites) was attempted but did not lead to any physically reasonable solutions. Complex magnetic orders with narrow temperature windows between successive

transitions are common in metallic rare earth compounds,<sup>21</sup> but are unusual in insulating rare earth–transition metal oxides.

The lattice distortions of  $Ba_3NdRu_2O_9$  evidently create a substantial anisotropy, as a large magnetic coercivity is observed at 2 K [Fig. 7(d)] and the reversal of magnetization proceeds via  $\frac{1}{3}$ -magnetization steps;  $\uparrow\uparrow\uparrow \rightarrow \uparrow\downarrow\uparrow \rightarrow \downarrow\downarrow\downarrow \rightarrow \downarrow\uparrow\downarrow \rightarrow \uparrow\uparrow\uparrow$  as magnetic field is cycled up  $\rightarrow$  down  $\rightarrow$  up. Two models for the  $\uparrow\downarrow\uparrow$   $\frac{1}{3}$ -magnetization phase are plausible—an order of  $2\uparrow:1\downarrow$ -spin chains parallel to the  $c$  axis, as observed in some frustrated triangular lattices such as  $CoV_2O_6$ ,<sup>22–24</sup> or an  $\uparrow\downarrow\uparrow$  order of successive Nd planes perpendicular to  $c$ . High-field neutron diffraction will be needed to distinguish between these possibilities.

## V. CONCLUSIONS

Ferromagnetic Ru spin dimers are present in  $Ba_3B'Ru_2O_9$  ( $B' = La, Nd, Y$ ), in contrast to antiferromagnetic dimers reported in other  $Ba_3B'Ru_2O_9$  types, evidencing an intradimer double exchange coupling. Antiferromagnetic order of the dimers breaks the degeneracy of the frustrated triangular lattice, but no accompanying lattice distortion is observed.  $Ba_3NdRu_2O_9$  is unique among the  $B' =$  rare earth series as it undergoes a structural distortion driven by  $Nd^{3+}$  crystal-field effects, and a separate ferromagnetic transition at lower temperatures. A substantial magnetic anisotropy leads to large coercivity and  $\frac{1}{3}$ -magnetization steps in the magnetic hysteresis of  $Ba_3NdRu_2O_9$  at low temperatures.

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