Frustration, strain and phase co-existence in the mixed valent hexagonal iridate Ba₃NaNr₂O₉

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Abstract
Using detailed synchrotron diffraction, magnetization, thermodynamic and transport measurements, we investigate the relationship between the mixed valence of Ir, lattice strain and the resultant structural and magnetic ground states in the geometrically frustrated triple perovskite iridate Ba₃NaNr₂O₉. We observe a complex interplay between lattice strain and structural phase co-existence, which is typically not observed in this family of compounds. The low temperature magnetic ground state is characterized by the absence of long-range magnetic order, and points towards the condensation of a cluster glass state from an extended regime of short range magnetic correlations.

Keywords: transition metal oxides, geometric frustration, iridates

(Some figures may appear in colour only in the online journal)

1. Introduction
Geometrically frustrated magnets—where triangular lattice antiferromagnets are considered to be an archetype—remain at the forefront of contemporary condensed matter [1–3]. Of particular interest in the recent years have been a number of ruthenium and iridium based perovskite variants which stabilize in an inherently frustrated environment. In general, the stabilization of a particular structural ground state depends on the tolerance limit of the corresponding symmetry which in turn is related to the relative ionic radii of the constituent elements. For instance, in the perovskite ABO₃, introducing a bigger element at the A and B sites can progressively tune the lattice from a high symmetry hexagonal to a lower symmetry orthorhombic, or even a monoclinic one [4]. The same is true for the double (A₂BBʹO₆) and triple layered perovskites (A₁BBʹ₂O₉) as well, where it has been shown that B site cations with higher atomic radii stabilize in a lower symmetry [5–7].

A relatively recent addition to these geometrically frustrated magnets are the barium based triple perovskite iridates of the form Ba₃MMr₂O₉ (M = alkali metal, alkaline earth metal, 3d transition metal or lanthanides). The choice of the M-site cation strongly determines the crystallographic symmetry, which in turn inordinately influences the magnetic ground states. For example, in M = Zn⁺⁺, a close realization of the elusive J = 0 state is observed whereas for M = Mg⁺⁺, Sr⁺⁺ and Ca⁺⁺, deviation from the non magnetic state in the form of antiferromagnetic exchange interactions, ferromagnetic and weak dimer like features are observed respectively [6]. Another addition to this family is the newly reported Ba₃CoIr₂O₉, where Co⁺⁺⁺⁺ being a magnetic ion strongly influences exchange paths leading to weak ferromagnetism at low temperature and the highest magneto-structural transition temperature reported in the triple perovskite iridates [8]. On the other hand, Ba₃BiIr₂O₉ has been reported to exhibit a giant magneto-elastic transition accompanied by the opening of a spin gap [9]. The structure-property relationships in these systems are clearly driven by a complex interplay between the relative strengths of competing spin–orbit coupling (SOC),...
Table 1. Room temperature crystal symmetry of the triple perovskite iridates of the form $\text{Ba}_3\text{M}\text{Ir}_2\text{O}_9$. Increasing the ionic radii of the $\text{M}$ site cation typically results in a lower symmetry, with $\text{M} = \text{Na}$ being a notable exception.

| Compound name       | Crystal symmetry | Ionic radii of $\text{M}$ ($\text{Å}$) | Ir valence | Magnetic ground state                                                                 |
|---------------------|------------------|----------------------------------------|------------|---------------------------------------------------------------------------------------|
| $\text{Ba}_3\text{CoIr}_2\text{O}_9$ | $P6_3/mmc$       | 0.65                                   | +5         | AFM ordering with $T_N = 107 \text{ K}$ [Phys. Rev. B 103 014437 (2021)]              |
| $\text{Ba}_3\text{MgIr}_2\text{O}_9$  | $P6_3/mmc$       | 0.72                                   | +5         | Antiferromagnetic exchange [Phys. Rev. B 97 064408 (2018)]                             |
| $\text{Ba}_3\text{ZnIr}_2\text{O}_9$  | $P6_3/mmc$       | 0.74                                   | +5         | Close realization of $J_{eff} = 0$ state [Phys. Rev. Lett. 116 097205 (2016)]        |
| $\text{Ba}_3\text{LiIr}_2\text{O}_9$  | $P6_3/mmc$       | 0.76                                   | +5.5       | AFM ordering with $T_N = 75 \text{ K}$ [J. Solid State Chem. 177 1493–1500 (2004)] |
| $\text{Ba}_3\text{CdIr}_2\text{O}_9$  | $C2/c$           | 0.95                                   | +5         | No ordering down to 2 K [Phys. Rev. B 100 064423 (2019)]                             |
| $\text{Ba}_3\text{NdIr}_2\text{O}_9$  | $C2/c$           | 0.983                                  | +4.5       | Ferromagnet, $T_C = 17.6 \text{ K}$ [J. Solid State Chem. 286 121309 (2020)]         |
| $\text{Ba}_3\text{CaIr}_2\text{O}_9$  | $C2/c$           | 1.00                                   | +5         | Weak dimer interaction [Phys. Rev. B 97 064408 (2018)]                                |
| $\text{Ba}_3\text{NaIr}_2\text{O}_9$  | $P6_3/mmc$       | 1.02                                   | +5.5       | Cluster glass state below 6 K [current manuscript]                                     |
| $\text{Ba}_3\text{SrIr}_2\text{O}_9$  | $C2/c$           | 1.18                                   | +5         | Ferromagnetic interactions [Phys. Rev. B 97 064408 (2018)]                             |

Figure 1. Main panel: fit to the Rietveld refinement of the synchrotron data at 295 K for $\text{Ba}_3\text{NaIr}_2\text{O}_9$. The compound crystallizes in a 6H-hexagonal perovskite structure with space group $P6_3/mmc$ (194). The calculated and the observed diffraction profiles are shown in red and black respectively. The vertical green lines indicates the Bragg positions and the brown line at the bottom is the difference between observed and calculated intensities. Inset: enlarged view of the higher angle peaks and the corresponding fit.

electronic correlation ($U$), and a hybridization interaction controlled by the Ir–O–Ir bond angle. Thus small perturbations, such as changes in lattice parameters caused by variations of different $M$ ions, can tip the balance between the competing energies and ground states. In all the reported 6H hexagonal perovskite iridates, the iridium radii of the $M$ site cation lies in the range of 0.605 Å–0.947 Å, beyond which the internal pressure forces the lattice to stabilize in a lower symmetry as shown in table 1. For example, the $\text{Ba}_3\text{CaIr}_2\text{O}_9$ system has been reported to stabilize in $C2/c$ monoclinic symmetry [5] which is in line with the expected structural ground state based on the tolerance limit. Interestingly, an exception appears to be the $\text{Ba}_3\text{NaIr}_2\text{O}_9$ system, which—in spite of the similar ionic radii of Na (1.02 Å) and Ca (1.00 Å)—has been reported to stabilize in the high symmetry hexagonal structure at room temperature [10]. In this report, we discuss this relatively un-investigated Na based triple perovskite iridate, where iridium is forced to be in the unconventionally high valence state of 5.5. We investigate polycrystalline specimens of this system using a combination of high resolution synchrotron diffraction, magnetization, resistivity and specific heat measurements. We observe that the lattice appears to accommodate strain as the temperature is reduced, which in turn precludes the stabilization of a lower symmetry structural phase. This is in contradiction to what is typically observed in this class of materials where the lattice prefers to stabilize in a lower symmetry on reducing temperature. On the other hand in $\text{Ba}_3\text{NaIr}_2\text{O}_9$, a very gradual and incomplete transformation to a low symmetry orthorhombic phase is observed, and the high symmetry hexagonal phase survives till the lowest measured temperatures. Measurements of the magnetization and specific heat point towards the existence of a extended cooperative paramagnetic regime characterized by short range magnetic correlations, which condenses into a cluster glass like state at low temperatures.
Figure 2. A schematic representation of the room temperature crystal structure of Ba$_3$NaIr$_2$O$_9$ along (a) the $a$-axis and (b) the $c$-axis. The iridium and sodium octahedra are depicted in blue and yellow respectively and the barium atoms are not shown for clarity. The black and green lines are guide to the triangular arrangement of iridium dimers in two different planes lying on top of each other. (c) The hexagonal crystal structure ($P6_3/mmc$) is extremely symmetric, with the sodium octahedra having an unique atomic position. Iridium has two different bonds associated with Ir face sharing and corner sharing O atoms shown in yellow and red colours for clarity. The bond lengths for these three different bonds are also depicted.

2. Experimental details

Polycrystalline specimens of Ba$_3$NaIr$_2$O$_9$ were synthesized by using the standard solid state reaction route. Stoichiometric amounts of high purity BaCO$_3$, Na$_2$CO$_3$ and IrO$_2$ were thoroughly ground and then sintered at 1100 °C. To avoid the possible loss of Na, the sample was only sintered in the pellet form and the synthesis was performed under excess oxygen environment to maintain the high oxidation state of iridium. The phase purity was confirmed by x-ray diffraction using a Bruker D8 advance diffractometer with a Cu K$_\alpha$ radiation. High resolution synchrotron x-ray diffraction data was collected using the materials science X04SA beam line (wavelength 0.565 26 Å) at the Swiss light source (SLS, PSI Switzerland). The finely ground powder was loaded in a glass capillary of diameter 0.3 mm and was spun during the data acquisition at various temperatures between 5 K and 300 K. The structure was analysed by Rietveld refinement using the FULLPROF suite [11, 12]. The structures shown in the manuscript are drawn using Vesta [13]. The homogeneity and stoichiometry of the compound were also confirmed by energy dispersive x-ray (EDAX) from ZEISS Ultra Plus. Magnetization and physical property measurements were performed using a quantum design (MPMS-XL) SQUID magnetometer and a physical property measurement system respectively.

3. Results and discussion

A Rietveld fit to the synchrotron diffraction data obtained at room temperatures is shown in figure 1 where Ba$_3$NaIr$_2$O$_9$ is seen to stabilize in the high symmetry hexagonal ($P6_3/mmc$) symmetry, and the lattice parameters are deduced to be $a = b = 5.86282(3)$ Å, $c = 14.61922(10)$ Å and $\alpha = \beta = 90^\circ; \gamma =$
120°. This is in good agreement with previous reports [14–17]. The room temperature structure is illustrated in figure 2(a) where Ir₂O₉ dimers (blue face sharing octahedra) are connected via corners to NaO₆ octahedra (in yellow). Figure 2(b) represents a projection along the crystallographic c-axis where IrO₆ octahedra forms a hexagonal ring around the NaO₆ octahedra. An expanded view of the Ir₂O₉ dimers (blue) and NaO₆ (yellow) is depicted in figure 2(c). All the Na–O bonds in the sodium octahedra are equivalent, whereas there are two different Ir–O bonds associated with face sharing and corner sharing oxygen atoms (yellow and red respectively) in the iridium octahedra. Since Na is in the +1 oxidation state, Ir is forced to stabilize in an atypical high oxidation state of +5.5. This refers to the combination of Ir⁵⁺ and Ir⁶⁺ within the dimers. Given that the hexagonal symmetry constrains iridium to a single atomic position, it can not form a charge ordered state. EDAX measurements were also used to confirm the stoichiometry. Since it is difficult to quantify the lighter elements (Na and O) using this technique, the atomic percentage ratio between heavy elements Ba and Ir was compared. The Ba:Ir ratio obtained from EDAX was observed to be 1.54 which is very close to the stoichiometric ratio of 3:2 = 1.5 expected from the chemical formula. A scanning electron micrograph image showed hexagonal facets that is a reflection of the underlying crystallographic symmetry.

A comparison of the temperature dependence of a few representative x-ray diffraction peaks as measured at the extreme temperatures of 5 K and 300 K is shown in figure 3(a). As the temperature is lowered, the diffraction peaks shift to higher angles and also becomes anisotropic. The modification of the peak profile could either signal the presence of strain in the lattice or a transformation to a lower symmetry phase. The former could be a consequence of the large ionic radii which Na possesses, whereas the latter has been reported in a number of triple perovskite iridates earlier. Since there were no additional peaks visible in the low temperature scan, the data was initially fit using a hexagonal model alone. These attempts were not successful, as is shown in the figure 3(b). Addition of strain using the broadening model available in FullProf made the fit better as can be seen in figure 3(c). This method is based on Stephens model [18] of anisotropic broadening, where the refinement of microstrain covariance parameters S₄₄₀, S₀₀₄ and S₁₁₂ corresponds to strain along the 100, 001 and 101 hkl planes. Though strain does appear to have an impact on the low temperature phase, the fitting was still not satisfactory enough, which hints at the possible presence of an additional low symmetry phase at low temperatures.

To identify the possible symmetry of the additional low temperature phase, existing literature in the ruthenate triple perovskite family was referred to, where multiple scenarios ranging from monoclinic (P2₁/c, C2/c) to orthorhombic (Cmcm), or even different structural models for the same compounds [19, 20] have been reported. After exploring all these possible options, the orthorhombic (space group- Cmcm (63)) phase [20] resulted in the best fit, with Rwp and Rp values of 3.24 and 2.47 respectively. The generated pattern was seen to match well with the high resolution synchrotron data as shown in figure 3(d). The lattice parameters obtained from the fit for the additional orthorhombic phase at 5 K are a = 11.6574(11) Å, b = 20.1975(21) Å, c = 14.5773(03) Å and α = β = γ = 90°. Figure 4 depicts this orthorhombic phase as viewed along the crystallographic c-axis. The black and green line indicates the triangular arrangement formed by Ir octahedra in alternate planes.

As was depicted earlier in figure 2(c), the hexagonal structure is characterized by highly symmetric octahedra with one unique bond length for Na and two (corresponding to the face sharing and corner sharing) for Ir. The lattice parameters a and b are equal, and is half the length of parameter c. On the other
Figure 4. (a) and (b) A schematic representation of the crystal structure of Ba$_3$NaIr$_2$O$_9$ along different axis using Vesta for the orthorhombic Cmcm phase. Here blue and yellow octahedra represents iridium and sodium respectively. The barium atoms are not shown for clarity. (b) Shows the hexagonal arrangement of the iridium octahedra made by two triangular units represented by the black dotted and green lines. (c) Schematic representation of the Ir dimers and the sodium octahedra is shown for the orthorhombic phase. A single Na–O and two unique Ir–O bonds splits into many different pairs of bonds after the structural transition. The different colours for oxygen denotes different atomic positions.

hand, in the orthorhombic space group, the lattice parameters $a$, $b$ and $c$ are drastically different. This low temperature C-centred orthorhombic symmetry is a $2a \times 2b$ primitive hexagonal pseudo-cell (or an ortho-hexagonal cell) and allows for three different crystallographic positions for Ir ($8f$, $8f$, $16h$) making it possible for the charge to be redistributed at these distinct cation sites. In addition, Na also now has three unique Wyckoff positions ($4a$, $4b$, $8d$) allowing for the movement of iridium while still maintaining the orthorhombic crystal framework. This is a complex low symmetry where each element has multiple unique positions as shown in figure 4(c), the details of which are given in [19]. A comparison of figures 4(c) and 2(c) highlights the major structural differences between these two phases. Since, the orthorhombic symmetry allows multiple positions for Na, Ir and O it leads to a highly distorted NaO$_6$ octahedra and Ir$_2$O$_9$ dimers as evident in figure 4(c). It can be clearly seen that a highly symmetric NaO$_6$ has now distorted into one with three different Na–O bond lengths. Similarly, the iridium dimer now consists of four different bond lengths compared with two in the hexagonal phase as shown in figure 2(c). We note that there have been prior reports of orthorhombic phases with only one crystallographic position for Ir, but attempts to fit the low temperature profile of Ba$_3$NaIr$_2$O$_9$ using this symmetry were not successful. Interestingly, in the ruthenium analogue, this need for multiple Ru positions was attributed to the presence of a charge ordered state [19].

It is observed that down to 50 K, a single structural hexagonal model with strain parameters is sufficient for the fitting. As a function of reducing temperatures, the phase fraction of hexagonal symmetry is invariant till 50 K, below which the orthorhombic symmetry is seen to stabilize, reaching 20% of the total volume fraction at 5 K (figure 5(a)). The temperature dependence of volume and $c/a$ ratio for the primary hexagonal phase are depicted in figures 5(b) and (c) respectively. Clearly, below 50 K, the $c/a$ ratio shows a change in slope associated with onset of the partial structural phase transformation. The evolution of the secondary orthorhombic phase is also evident in the temperature dependence of the microstrain covariance parameters as in depicted in figure 5(d). The strain parameters $S_{400}$ and $S_{004}$ show a sharp change close to the structural transformation temperature and remains almost constant below it, whereas the parameter $S_{112}$ increases dramatically. These changes in the microstrain parameters are indicative of deviations in the $\alpha$ and $\beta$ angles of the hexagonal lattice framework, and consistent with a distortion towards an orthorhombic symmetry. It is interesting to note that the emergence of the secondary orthorhombic phase at low temperatures is not associated with the observation of a splitting of the hexagonal peaks, as was observed in an earlier report on the same system [21]. These authors [21] reported that their x-ray diffraction data indicates a hexagonal to monoclinic distortion below 200 K. However, they also stated that the pattern at 200 K could possibly be fit by a lower symmetry due to the larger number of refinable parameters. Moreover, in their fitting procedure, the iridium and sodium at atomic displacement parameters shifted to physically unfeasible negative values, and had to be artificially fixed (and left unrefined) during the analysis procedure. This places reasonable doubt on the validity of the claim that a $P6_3/mmc$ to $C2/c$ transition occurs.
Figure 5. (a) The variation of the phase fraction of the hexagonal $P6_3/mmc$ with temperature. As the temperature reduces, the hexagonal phase converts slowly to orthorhombic phase, nucleating at 50 K and reached 80% of the total volume fraction at 5 K. Temperature evolution of the (b) volume, (c) ratio of lattice parameters $c/a$ for the hexagonal symmetry. A slight variation in both the parameters are observed marking the onset of the lower symmetry orthorhombic phase. (d) The temperature dependence of the microstrain parameters $S_{HKL}$ for three different hkl is depicted. The sharp change in $S_{000}$ and $S_{004}$ close to the structural transformation temperature is consistent with distortions of the lattice with the onset of orthorhombic symmetry.

close to 200 K. As they themselves state, the structural transition probably occurs at a lower temperature, and clear peak slitting is only seen at around 100 K. In addition, their single crystal diffracted strongly from 300 K to 200 K, but below this temperature, the quality of the data degraded markedly. The diffraction quality was regained once the system was heated up to room temperature again. This is consistent with what would happen if the lattice accommodates an inordinate amount of strain and is also suggested through the synchrotron diffraction studies of the present work.

We note that there are significant differences in our inferences, in comparison to what was reported earlier. One of the possible reasons for this disparity could be the different synthesis protocols and microstructures, which lead to different strain dynamics in the system. In our case, this incipient strain not only masks the peak splitting expected due to the orthorhombic distortion by causing excess anisotropic peak broadening, but also results in an incomplete conversion of the high temperature hexagonal phase to the lower symmetry orthorhombic one. In general, many of the triple perovskite iridates have been reported to exhibit a first order phase transition from hexagonal to orthorhombic, monoclinic etc. In the present system, the lack of such a transition stems from the presence of Na at the $M$ site in $Ba_3MIr_2O_9$. The valence state and ionic radii of Na provides an ideal environment for the hexagonal lattice framework and therefore, the first order transition which is expected to manifest as a function of reducing temperature is missing. In addition, various competing energy scales like crystal field splitting, SOC, on-site Coulomb interaction, and Hund’s coupling also influences the ground state. For instance, in $Ba_3ZnIr_2O_9$, where Zn is non magnetic, the lattice prefers to stay in the $P6_3/mmc$ space group till the lowest temperature measured. Since, Na offers less Coulomb repulsion compared to other
iridates with magnetic \( M \) sites like Co, Bi, etc, the lattice prefers to stay in the hexagonal framework. However, as the temperature is lowered, the Coulomb repulsion increases as the volume decreases. This leads to the development of strain in the lattice, which is released by a partial transformation to a phase with a lower symmetry.

Figure 6(a) shows the temperature dependence of the magnetic susceptibility of \( \text{Ba}_3\text{NaIr}_2\text{O}_9 \) as measured at an applied field of 500 Oe. The susceptibility increases with decrease in temperature with the zero field cooled (ZFC) and field cooled (FC) curves diverging close to 6 K as shown in figure 6(b), indicating the presence of a glass transition. This is at variance with what has been reported in early single crystalline specimens of this system, where features in the magnetization were observed at 75 K and 50 K \( [10, 21] \). Since iridium is the only magnetic ion in this system, the magnetic moment arises from the charge balance between \( \text{Ir}^{4+} \) (5d\(^+\)) and \( \text{Ir}^{5+} \) (5d\(^5\)). Based on these oxidation states and the octahedral coordination environments, the theoretical spin-only moment for non-interacting mixed valent \( \text{Ir}^{4+} \) (5d\(^+\)) and \( \text{Ir}^{5+} \) (5d\(^5\)) is 6.7 \( \mu_B \) per formula unit. It is to be noted that \( \text{Ir}^{5+} \), by virtue of its electronic configuration (5d\(^5\)) and under the influence of strong SOC (\( t_{2g}^2 \text{cub} \)) is also expected to exhibit a \( J = 0 \) non-magnetic state and in that case, the magnetic contribution should come from \( \text{Ir}^{4+} \) alone in the \( \text{Ba}_3\text{NaIr}_2\text{O}_9 \) system. However, a breakdown of the \( J = 0 \) state has been observed previously in systems like \( \text{Ba}_2\text{ZnIr}_2\text{O}_9 \) \( [22] \) and \( \text{Ba}_2\text{MgIr}_2\text{O}_9 \) \( [6] \), where the Ir moment was reported to be 0.2 \( \mu_B \) and 0.5–0.6 \( \mu_B \) respectively although the electronic configuration for iridium was \( \text{Ir}^{4+} \) (5d\(^+\)) and a \( J = 0 \) state was expected. A defining feature of these triple perovskites is the presence of \( \text{Ir}_2\text{O}_8 \) dimers in the backdrop of strong SOC. It has been suggested that inter and intra dimer interactions are strongly influenced by the local distortions creating complex \( \text{Ir}–\text{O}–\text{Ir} \) pathways leading to the breaking of degenerate \( t_{2g}^2 \) levels. Under the influence of strong SOC, these states reform into mixed \( J \) states, which in turn facilitate hopping induced superexchange interactions that result in a finite magnetic moment at the \( \text{Ir}^{4+} \) site. Our fits yield a value of 3.42(5) \( \mu_B \) per formula unit for the \( \text{Ba}_3\text{NaIr}_2\text{O}_9 \) system. This is close to the reported magnetic moments of 3.6 \( \mu_B \) per formula unit reported earlier in \( \text{Ba}_3\text{NaIr}_2\text{O}_9 \) and 3.93 \( \mu_B \) per formula unit reported for \( \text{Ba}_3\text{LiIr}_2\text{O}_9 \) \( [10] \). Such reduction in moment is a peculiar feature seen in iridates and has been reported for a wide range of iridium based oxides \( [6, 23–25] \). The strong suppression of the overall magnetic moment is ascribed to the joint effect of spin orbit interaction and strong covalency, resulting in the formation of metal–metal bonds. They act against the intraatomic Hund’s rule exchange interaction to reduce the total magnetic moment on the iridium dimer. This was further confirmed by our synchrotron measurements where an anomalous shortening of Ir–Ir bond distance in the +5.5 valence state (2.73 Å) as compared to the +5 state (2.75 Å) corroborates the formation of the metal–metal bonds.

A recent report on a member of the triple perovskite family \( \text{Ba}_3\text{CoIr}_2\text{O}_9 \) \( [8] \) further highlights the role of the inter and intra dimer interactions between Ir ions on the magnetic ground state of the system. The schematic representation of the hexagonal crystal structure \( P6_3/mmc \) is shown in figure 7(a). The yellow and blue octahedra represent cobalt or sodium and iridium respectively. The barium ions are not shown for clarity. The symbols \( J_1, J_2 \) and \( J_3 \) represents superexchange pathways where \( J_1 \) and \( J_2 \) denotes intra and inter dimer interactions respectively along the \( c \)-axis and \( J_3 \) represents inter dimer interactions in the \( ab \) plane. Both these compounds, \( \text{Ba}_3\text{CoIr}_2\text{O}_9 \) and \( \text{Ba}_3\text{NaIr}_2\text{O}_9 \), have the same (high temperature) hexagonal crystal symmetry but cobalt, being a magnetic ion, offers additional superexchange pathways for iridium to interact along the \( ab \) (\( J_3 \)) as well as along the \( c \)-axis (\( J_1 \) and \( J_2 \)) as shown in figure 7(a). Since Na is non-magnetic, these superexchange pathways are absent and thus in this case the Ir dimers are separated from each other via non magnetic Na octahedra (yellow). In the absence of these intra dimer superexchange paths, the extended superexchange pathways offered by Ir–O–O–Ir, marked by dotted lines (black and yellow) could possibly influence the magnetic exchange interactions. Similar extended superexchange interactions are present.
in the orthorhombic phase of this compound as shown by blue dotted lines in figure 7(b). Thus, in addition to metal–metal bonds, the presence of super exchange and extended super exchange interactions pathways lead to complex magnetic exchange interactions in these systems.

Though heat capacity measurements did not show evidence of any long range ordered state, a Curie Weiss fit of the inverse magnetic susceptibility was valid only in temperatures in excess of 260 K, indicating the presence of an extended regime of short range magnetic correlations. To gain further insight into the extent of this regime, we performed temperature dependent measurements of the thermo-remanent magnetization (TRM), which has proven to be an effective tool in the investigation of magnetically frustrated systems. A TRM measurement performed on the Ba$_3$NaIr$_2$O$_9$ system in a cooling field of 1 kOe is depicted in figure 6(e). Two precipitous jumps are clearly observed—one below 10 K, which corresponds to the low temperature magnetic transition observed in the ZFC–FC measurements, and one just below 175 K, which roughly corresponds to the region where the inverse magnetic susceptibility deviates from the linear Curie–Weiss fit. In the absence of long range order, this feature at high temperature could be ascribed to the onset of a cooperative paramagnetic regime. First coined by Villain [26], cooperative paramagnetism was used to describe the low temperature dynamics of a classical Heisenberg spins on a corner sharing tetrahedral framework, and is a defining feature of systems with high geometric frustration. Cooperative paramagnetism is seen in many transition metal oxides which crystallizes in magnetic spin configurations that are geometrically or topologically prone to frustration due to underlying lattices based upon corner, edge or face sharing triangles or tetrahedra. A wide range of systems including pyrochlore, spinels, and jarosites are now known to exhibit this phenomena [27–29]. This state can also be looked upon as being analogous to the Griffiths phase [30], with the notable difference that the low temperature magnetic ground state instead of being magnetically ordered, now undergoes a glass-like dynamical phase transition. We believe that the nucleation of finite size correlated regions within the antiferromagnetic matrix starts to develop close to 175 K. As the temperature reduces, magnetic frustration develops due to competing intra dimer (nearest neighbour $J_1$) and inter dimer (next-nearest neighbour $J_2$ and $J_3$) interactions. The absence of conventional long range antiferromagnetic order is due to the interplay between frustration and quenched disorder. As proposed by Imry and Ma [31], a random quenched disorder inhibits the transition to a long range magnetically ordered state but instead favours the nucleation of correlated magnetic clusters [32].
In Ba₃NaIr₂O₉, the hexagonal phase is highly frustrated, with IrO₆ octahedra sitting in a triangular network. This does not allow the iridium dimers to order magnetically, and they presumably remain paramagnetic. This can also be inferred from a literature survey (table 2) of triple perovskite iridates, where the compounds of the form Ba₃M(Ir/Ru)₂O₉ (M being a non-magnetic ion) that stabilize in the hexagonal phase have been reported to remain paramagnetic. Clearly, in these triple perovskites, the magnetic ground state is critically influenced by the structural symmetry. We believe that the orthorhombic phase is more magnetic, as the release in frustration can allow the Ir dimers to order antiferromagnetically. The cluster glass phase that we observe in Ba₃NaIr₂O₉ appears to emerge from the coexistence of both these phases. The partial conversion of the hexagonal phase into an orthorhombic one leads to the formation of small phase separated orthorhombic regions. These small orthorhombic regions or clusters have antiferromagnetic ordering and are embedded in a paramagnetic background provided by the hexagonal phase. The size/number of these regions changes with the phase fraction in orthorhombic phase and since the majority phase is always hexagonal, they fail to coalesce into long range magnetic order and eventually freezes in a cluster glass like phase at low temperatures.

The temperature dependence of the heat capacity as measured from 2–250 K is depicted in figure 6(c). Clearly, the low temperature anomaly observed in magnetization is absent here which implies that the change in entropy is rather small. Figure 6(d) shows the temperature dependence of reciprocal magnetic susceptibility (1/χ). Interestingly, a linear region was observed well in excess of 200 K, and hence only the temperature range 260–300 K was chosen to fit the inverse magnetic susceptibility using the Curie–Weiss law. An effective magnetic moment value 3.42(5) μB per formula unit and a Weiss temperature (θc) of −285.36(1.1) K were obtained, with the latter being indicative of the extent of frustration in this system, since we only observe a feature in magnetization at 6 K.

Interestingly, the high temperature magnetic feature (~175 K) which we observe in the TRM measurements is not easily discernible in other measurements, and hence has gone unreported in prior single crystal measurements of Ba₃NaIr₂O₉ as well [10]. This is a consequence of the fact that the magnetic susceptibility of the paramagnetic matrix (χPM) would be of the same order (or even larger) than that of the antiferromagnetic clusters (χAFM), making it difficult to unambiguously determine the contribution of the antiferromagnetic clusters in traditional in-field magnetic measurements. On the other hand, since TRM is a zero-field measurement, the contribution of the paramagnetic magnetic susceptibility is likely to be suppressed, allowing for one to identify more clearly the temperature regime at which the antiferromagnetic clusters begin to nucleate. Interestingly, the ruthenate analogue of this triple perovskite was reported to exhibit the opening of a charge gap at 210 K [19], though we do not observe any evidence of a similar phenomena in its iridium counterpart investigated here. The magnetic transition in these family of oxides is typically associated with a symmetry breaking lattice distortion which alters the exchange parameters, thereby neutralizing the frustration. In the case of Ba₃NaIr₂O₉, the interesting capacity of the system to accommodate strain impedes a traditional structural transformation. Therefore, rather than observing a first order transition from hexagonal symmetry to an orthorhombic one, we observe a slowly evolving strained lattice gradually transforming to a lower symmetry where the major phase still retains the original high temperature symmetry. A strained lattice of this nature is probably closer to the reports of the triple perovskite family when subjected to external pressure [5, 35]. For instance on application of pressure, the Ba₃NaRu₂O₉ transforms to a new phase, 3C₁₂ᵢ–Ba₃NaRu₂O₉, where the charge gap completely disappears and Pauli paramagnetism emerges, possibly as a consequence of strong electron–electron correlations. The Ba₃CaRu₂O₉ system has also been reported to exhibit excess strain in the lattice, in the form of peak broadening as the temperature was lowered. Therefore, the ground state in Ba₃NaIr₂O₉ is clearly influenced by the complex interplay of a mixed valent Ir, frustration, phase coexistence and strain.

The temperature dependence of the electrical resistivity is shown in the figure 8. The system is semiconducting in nature, with the magnitude of resistivity changing by four orders of magnitude from its room temperature value. Attempts to fit using the Arrhenius model and Efros–Shklovskii variable range hopping model were unsuccessful. A better fit was
obtained by using the Mott variable-range hopping (VRH) model which is given by:

\[ \rho \propto \exp((T_0/T)^\nu), \tag{1} \]

where the best fits were obtained for \( \nu = 1/3 \) indicating VRH in two dimensions [36]. The magnetic Ir dimers are connected via non-magnetic Na octahedra, generating a pseudo 2D structure. Thus, the crystal structure of this triple perovskite can be expressed by alternate stacking of two kinds of 2D layers which consist of the NaO6 octahedra and the Ir2O9 polyhedra. This may account for the observed 2D resistivity behaviour. The resistivity of Ba3NaIr2O9 as a function of \( \ln \rho \) vs \( T^{-0.33} \) is shown in the inset of figure 8. The localization of states due to strong Coulomb interactions and slight structural disorder would be consistent with VRH behaviour. The resistivity of the ruthenate analogues of the triple perovskites Ba3MRu2O9 (R = Fe, Co, Ni, Cu, In, Ln), all follows the same characteristics [37, 38]. In general, the antiferromagnetic state is likely to be more insulating than the paramagnetic one. We also note that the orthorhombic state in many of these triple perovskites have been reported to exhibit charge ordering, leading to drastic decrease in conductivity. This has been reported, for instance, in the ruthenate analogue of this compound [19]. Due to the small percentage of the orthorhombic phase, we were not able to observe a drastic jump as has been seen for Ba3NaRu2O9, though one cannot rule out the possibility of a similar charge ordered state within the orthorhombic phase at low temperatures.
In addition to frustration, the presence of mixed valent states of iridium and phase co-existence sets the stage for inhomogeneous magnetic exchange interactions. The observation of an anomaly below 6 K in the \( M(T) \) curves indicates the emergence of glassy dynamics owing to this frustration. However, the signal was too small for us to clearly identify a frequency dependent peak in the ac susceptibility measurements. Another method to probe glassy dynamics is to use the time evolution of isothermal remanent magnetization (IRM). This involves cooling the sample from 300 K to 2 K in the presence of a magnetic field, after which the magnetic field is switched off and the decay of magnetization is measured as function of time. A special formulation of power law is known to study the time dynamics of magnetization for glasses under stress known as the Kohlrausch Williams Watt (KWW) stretched exponential equation [39–41] given by:

\[
m(t) = m_0 - m_g \exp\left\{-(t/\tau)^\beta\right\},
\]

where \( m_0 \) is related to initial remanent magnetization, \( m_g \) is magnetization of glassy component, \( \tau \) and \( \beta \) are the characteristic relaxation time constant and stretching exponent respectively. Here \( m(t) \) is representative of the sum of many exponential decays weighted by a distribution of individual relaxation times, with the magnitude of \( \beta \) indicating the breadth of that distribution [42]. The value of \( \beta \) has been reported to lie between 0 and 1 for a wide range of disordered systems. The normalized magnetization \( m(t) = (M_t/M_{t=0}) \) as measured in \( \text{Ba}_3\text{NaIr}_2\text{O}_9 \) at 2 K with cooling fields of 500 Oe (main panel) and 1 T (inset) is plotted in figure 9. As depicted by the blue curve, the fit to a simple power law was not satisfactory. However, a good fit was obtained for the KWW model and the resultant values of \( \beta \) are 0.518(14) and 0.5464(68) for 500 Oe and 1 T respectively. These values are in line with the reported values for cluster glass phase in many double perovskites [32, 43], and reinforces our contention that the low temperature magnetic ground state is one which has magnetically frozen clusters.

The magnetic interactions in \( \text{Ba}_3\text{NaIr}_2\text{O}_9 \) are predominantly antiferromagnetic, though, signatures of the presence of mixed magnetic interactions are suggested by a weak loop opening in magnetization isotherms at 2 K as shown in figure 10. As revealed by our synchrotron studies, the low temperature structure comprises of a highly strained lattice with two unique structural motifs coexisting. This coupled with the existence of finite size antiferromagnetic clusters allow for exchange bias, with the antiferro and ferro-magnetic contributions arising from the magnetic order within ordered clusters and uncompensated spins at the surface of these clusters respectively (figure 10). The presence of a low temperature glass-like magnetic ground state is also evidenced in a strong upturn in \( C/T \) vs \( T \) figure 11, with a clear deviation from what is expected from Debye’s law. This excess entropy arises as a consequence of the glassy dynamics [44], and appears to be a signature common to structural and magnetic glasses. This is also evident on plotting \( C/T \) vs \( T^2 \) curve, indicating the presence of an excess entropy that releases as a consequence of short range ordering. The inset of figure 11 shows the fit to the low temperature \( C/T \) vs \( T^2 \) curve. The data is fitted using the expression \( C_p = \gamma T + \beta T^3 \) where \( \gamma \) and \( \beta \) are related to the electronic and vibrational degrees of freedom respectively. We also calculated the Debye temperature \( \theta_D \), which is derived from the expression, \( \theta_D = (12\pi^4 p R/5\beta)^{1/3} \), where \( R \) is the ideal gas constant and \( p \) is the number of atoms per formula unit. The calculated value of \( \theta_D \) is 236.84 K. The obtained values of \( \gamma \) and \( \beta \) are 77 mJ mol\(^{-1}\) K\(^{-2}\) and 2.19 mJ mol\(^{-1}\) K\(^{-4}\) T\(^{-1}\) respectively. The high value of \( \gamma \), unusual for insulating systems, can be attributed to the inherent disorder which affects the spin, charge and orbital degrees of freedom. This has
been previously observed in insulating triple perovskite iridate (Ba$_3$ZnIr$_2$O$_9$-25.9 mJ mol$^{-1}$ K$^{-2}$), and manganites [22, 45]. The high value observed here signifies the excess entropy imparted by the frustration and disorder in this oxide owing to the mixed valence state and stress. Interestingly, on the application of a moderate magnetic field (0.5 T), no change in the heat capacity was observed (not shown here), which suggests against the presence of paramagnetic impurity centres [46, 47].

4. Summary

In summary, we report on the structure-property relationship in the mixed valent geometrically frustrated triple perovskite iridate Ba$_3$NaIr$_2$O$_9$. In contrast to what is expected from purely structural considerations, this system stabilizes in a high symmetry hexagonal structure at room temperatures. On reducing the temperature, the lattice prefers to be strained rather than distort to a low symmetry phase, as is the norm in this family of materials. Though a low symmetry orthorhombic phase is finally nucleated below 50 K, this conversion is only partial of materials. Though a low symmetry orthorhombic phase is finally nucleated below 50 K, this conversion is only partial. On further cooling the lattice prefers to be strained rather than distort to a low symmetry phase, as is the norm in this family of materials.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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