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Magnetism in cation-disordered $3d$-$4d$/$5d$ double perovskites

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Employing an exact diagonalization Monte Carlo solution of the first-principles-derived model Hamiltonian of a number of $A_2BB'O_6$ double-perovskite compounds, containing a $3d$ transition metal at the B site and a $4d$ or $5d$ transition metal ion at the B' site, we investigate the effect of B/B' cation disorder on their magnetic properties. Our exhaustive study reveals that the influence of cation disorder on both the magnetic transition temperature and magnetization depends strongly on the underlying exchange mechanism with a distinct difference between the double exchange mechanism and a combined double exchange and superexchange mechanism. We further find that the nature of the disorder has a remarkable effect. While the uncorrelated or random disorder has a severely detrimental effect, especially for magnetism having a superexchange contribution, correlated disorder with a high degree of short-range order retains the magnetic properties of the fully cation-ordered compounds to a large extent. Our findings shed light on the puzzling report of magnetic order in fully cation-disordered CrRu oxides.

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Introduction. Double perovskites (DPs) containing two transition metal (TM) ions instead of a single TM ion as present in the widely studied simple perovskite structure, have created significant interest in recent times due to their intriguing magnetic properties [1]. DPs synthesized with a choice of transition metals, one from a $3d$ TM series and another from a $4d$ or $5d$ TM series, have been reported to exhibit magnetic transition temperatures ranging from ≈200 to ≈800 K [2].

The general formula of DPs is given by $A_2BB'O_6$, which can be derived by doubling the simple perovskite formula of ABO_3, replacing one of the two B cations in the $A_2B_2O_6$ formula by another B' cation, and alternately ordering B and B' cations, as shown in the left panel of Fig. 1. The perfect ordering of B and B' cations, however, is an idealized situation. In reality, the presence of B/B' disorder, commonly known as antisite disorder (ASD), where a certain fraction of the B and B' pair gets interchanged in a perfectly ordered arrangement, is inevitable [3–5]. Therefore, it is a matter of great concern to what extent ASD affects the fascinating magnetic properties of the DPs.

This discussion became more intriguing after the report of magnetic ordering with a high transition temperature of more than 400 K [6] in a CrRu-based system in which apparently no Cr/Ru cation order was observed. No cation order would amount to 50% ASD [7]. As pointed out in Ref. [6], any superexchange mechanism in the presence of antisite disorder would suppress magnetism with the transition temperature dropping off rapidly and in extreme cases of 50% ASD may lead to spin-glass-like behavior. It is thus very surprising to find even this extreme disorder is not able to suppress magnetism. Rather, it supports magnetism at temperatures higher than room temperature. What is the clue to this puzzle?

The problem of the cation disordering effect in the magnetism of $3d$-$4d$/$5d$ DPs is complex due to multiple reasons. First, as discussed in Refs. [8,9], magnetism in DPs such as Sr_2FeMoO_6 is given by the two-sublattice double-exchange mechanism operating between the core spin of the Fe ion and the itinerant electron delocalized over the Fe-O-Mo network, thereby stabilizing the parallel alignment of Fe core spins. Later on, this mechanism is found to be operative in a number of $3d$-$4d$/$5d$ DPs [10–13]. The influence of disorder on such a double-exchange-driven mechanism, which depends on the relative positioning of B-site levels and B'-O hybridized levels, is expected to be distinct from that arising due to the commonly assumed superexchange mechanism. Second, the magnetism in a certain class of $3d$-$5d$ DPs has been reported to be contributed by the combined effect of a double-exchange (DE) and superexchange (SE) mechanism [11], making the situation more complex. Third, it is to be noted if two $3d$ TM ions with a large core spin are on neighboring sites in an antisite-disordered situation, the nearest-neighbor B-B antiferromagnetic (AFM) coupling becomes operative, which would be competitive with the two-sublattice DE-driven parallel alignment of B core spins. Fourth, the effect should also depend on the nature of ASD. The ASD can be placed randomly throughout the lattice, leading to a homogeneous distribution of defects, or they can appear as a patchy structure with locally ordered domains, separated by antiphase boundaries (APBs), as shown in the middle and right panels of Fig. 1, respectively. X-ray absorption fine structure (XAFS)

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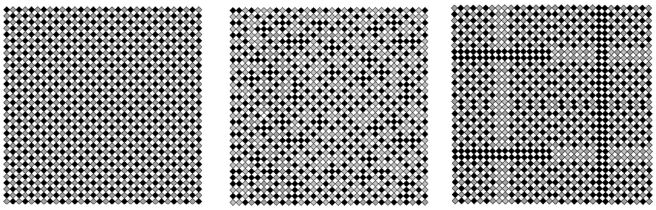

FIG. 1. Left panel: Schematic view of in-plane projection of rocksalt ordering of BO_6 (black) and $B'O_6$ (gray) octahedra in DP. Middle panel: The same, but in the presence of random ASD. Right panel: The same, but in the presence of correlated disorder, with well-defined domains, separated by APB.

[14] or electron microscopy experiments [15] carried out on Sr_2FeMoO_6 (SFMO) DPs strongly support the dominance of a patchy structure formation over random distributions.

Although there have been attempts to theoretically study the disordering effect [16,17], a comprehensive microscopic investigation including all the aspects discussed above is lacking. In this Rapid Communication, we do so by using a multipronged approach of combining first-principles density functional theory (DFT) calculations to derive a compound-specific model Hamiltonian together with an exact diagonalization Monte Carlo (ED-MC) solution of a model Hamiltonian to obtain the finite-temperature magnetic properties. Our study, encompassing a rather large set of six different known $3d$-$4d/5d$ compounds, is expected to provide a general picture of the cation-disordering effect on the magnetism of $3d$-$4d/5d$ DPs. This in turn should also yield a solution to the CrRu puzzle.

Exchange mechanism in 3d-4d/5d DPs. As mentioned already, the magnetism in a number of $3d$-$4d/5d$ DPs is found to be driven by a novel hybridization-mediated mechanism [8–13]. This mechanism originates from the large exchange splitting at the $3d$ TM in the B site and the strong hybridization between the B' states and states at the B site, which results in an induced negative spin splitting at the B' site when the B' energy levels lie within the exchange split levels of the B site. This essence is summarized schematically in Fig. 2 (scenario 1). However, while the magnetism in compounds such as Sr_2FeMoO_6 (SFMO) [10], Ba_2FeReO_6 [12], Sr_2CrWO_6 (SCWO) [11], etc., turned out to be solely driven by the above described hybridization-mediated mechanism, in the case of double perovskites such as Sr_2CrReO_6 (SCReO) and Sr_2CrOsO_6 (SCOO) [11], an additional contribution comes into play which arises due to the intrinsic spin splitting of the B' states which adds on to the induced B-B' hybridization-driven spin splitting at the B' site (scenario 2). The most general form of the model Hamiltonian applicable for all $3d$-$4d/5d$ DPs thus can be written as [11]

$$\begin{aligned}H &= H_{\rm DE} + H_{\rm SE}\\ &= \epsilon_B \sum_{i\in B} c^\dagger_{B,i\sigma} c_{B,i\sigma} + \epsilon_{B'} \sum_{i\in B'} c^\dagger_{B',i\sigma} c_{B',i\sigma}\\ &\quad + t_{B\text{-}B'} \sum_{\langle ij\rangle\sigma} c^\dagger_{B,i\sigma} c_{B',j\sigma} + J \sum_{i\in B} \mathbf{S}_i \cdot c^\dagger_{B,i\alpha} \vec{\sigma}_{\alpha\beta} c_{B,i\beta}\\ &\quad + J_2 \sum_{i\in B, j\in B'} \mathbf{S}_i \cdot \mathbf{s}_j, \end{aligned} \tag{1}$$

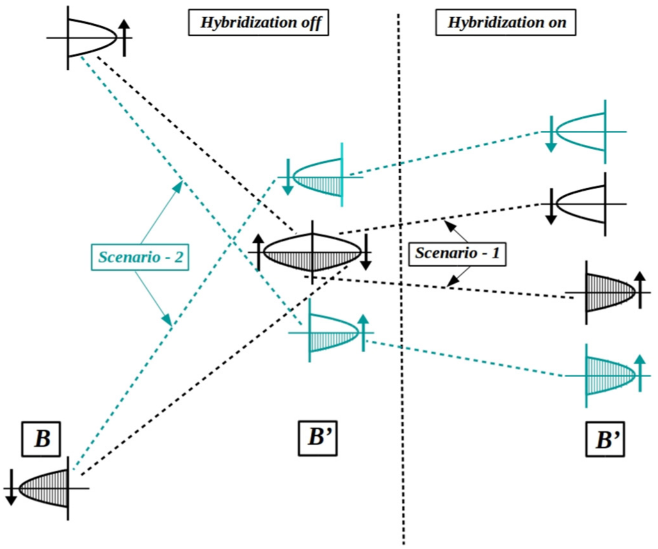

FIG. 2. The two possible scenarios of driving mechanisms of exchange in $3d$-$4d/5d$ DPs.

where the first four terms of the Hamiltonian describe the hybridization-driven mechanism of exchange, resulting in a two-sublattice double-exchange Hamiltonian ($H_{\rm DE}$) consisting of (a) a large core spin of a $3d$ TM B site ($\mathbf{S}_i$) considered to be a classical spin, (b) an effective hybridization between B and B', decided by the on-site energies (ϵ_B, $\epsilon_{B'}$) and hopping integral ($t_{B\text{-}B'}$), which gives rise to delocalization of the itinerant electron over the B-B'-O network, and (c) strong coupling between the core spin $\mathbf{S}_i$ at the B site and the itinerant electron through a coupling, $J \gg t_{B\text{-}B'}$. The last term of the Hamiltonian ($H_{\rm SE}$) expresses the SE interaction coupling (J_2) between the large core spin $\mathbf{S}_i$ at the B site, and the intrinsic spin at the B' site ($\mathbf{s}_j$), which is antiferromagnetic in nature. Note $H_{\rm SE}$ would be operative for systems such as SCReO or SCOO, and would be absent for SFMO or SCWO.

Given the fact that $J \gg t_{B\text{-}B'}$, the Hamiltonian in Eq. (1) can be cast into a form appropriate for $J \to \infty$, having spinless fermionic degrees of freedom at the B site, and itinerant electrons having both spin channels [18], as given below,

$$\begin{aligned}H &= \epsilon_{B'} \sum_{i\sigma} c^\dagger_{B',i\sigma} c_{B',i\sigma} + \tilde{\epsilon}_B \sum_i \tilde{c}^\dagger_{B,i} \tilde{c}_{B,i}\\ &\quad + t_{B\text{-}B'} \sum_{\langle ij\rangle} \left(\sin\frac{\theta_i}{2} \tilde{c}^\dagger_{B,i} c_{B',j\uparrow} - \cos\frac{\theta_i}{2} e^{i\phi_i} \tilde{c}^\dagger_{B,i} c_{B',j\downarrow} \right)\\ &\quad + J_2 \sum_{i\in B, j\in B'} c^\dagger_{B',j\alpha} \vec{\sigma}_{\alpha\beta} c_{B',j\beta} \cdot \vec{S}_i. \end{aligned} \tag{2}$$

θ and ϕ dictate the relative alignment of core spins in the B sublattice. While the above Hamiltonian is sufficient for a description of the perfectly ordered compound, for the disordered compound, additional terms are needed for the description of antisite regions, as given below,

$$\begin{aligned} H_{\rm disord} = {} & t_{B\text{-}B} \sum_{\langle ij \rangle} \left[\cos\frac{\theta_i}{2} \cos\frac{\theta_j}{2} \right. \\ & \left. + e^{i(\phi_j - \phi_i)} \sin\frac{\theta_i}{2} \sin\frac{\theta_j}{2} \right] \tilde{c}^{\dagger}_{B,i} \tilde{c}_{B,j} \\ & + t_{B'\text{-}B'} \sum_{\langle ij \rangle \sigma} c^{\dagger}_{B',i\sigma} c_{B',j\sigma} + J_{\rm AS} \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j, \end{aligned} \quad (3)$$

where $J_{\rm AS}$ is an antiferromagnetic B-B antisite superexchange, and $t_{B\text{-}B}$ and $t_{B'\text{-}B'}$ are the nearest-neighbor B-B and B'-B' hoppings that arise in the presence of ASD. The complete Hamiltonian was solved using the ED-MC technique, the Hamiltonian H ($H_{\rm disord}$) being used in the ordered (disordered) region. The classical spins $\mathbf{S}_i$ at the B sites were updated using the Monte Carlo simulation. In each configuration of core spins, the above-mentioned fermionic Hamiltonians were diagonalized and the total energy was calculated. The calculated total energy was subsequently used to choose the B-site spin configurations within the Metropolis algorithm. For details, see the Supplemental Material (SM) [19].

Realistic model Hamiltonian. To obtain a material-specific description, the input parameters of the model Hamiltonian $\epsilon_B, \epsilon_{B'}, t_{B\text{-}B'}, J_2$ need to be evaluated. In order to provide realistic estimates of $\epsilon_B, \epsilon_{B'}, t_{B\text{-}B'}$, we carried out muffin-tin orbital (MTO) [20] based Nth-order MTO (NMTO)-downfolding calculations [21] to derive a low-energy Hamiltonian starting from non-spin-polarized DFT calculations, and reading off the on-site and off-site matrix elements of the real-space representation of the low-energy Hamiltonian [13]. The details can be found in SM. The derived parameters are thus expected to capture the correct structural and chemical information of the compounds under consideration. We have considered a total of six different 3d-4d/5d DPs, with Fe or Cr at the 3d site, which have been studied most extensively, namely, SFMO, Sr_2CrMoO_6 (SCMO), SCWO, SCReO, SCOO, and Ca_2CrWO_6 (CCWO). DFT calculations [10,11,13] as well as experimental investigations [9,22–26] in all these cases reveal that the B cation is in a nominal 3+ valence state, which means a d^5 configuration for Fe and a d^3 configuration for Cr. This puts the 4d/5d B' cation in a nominal 5+ valence state. The minimal, low-energy Hamiltonian was thus constructed by retaining all five d orbitals of Fe, only t_{2g} orbitals in the case of Cr, and 4d/5d ions such as W, Re, Os, and Mo. The extracted parameters, some of which have been taken from our existing work [10,11,13], and some of which have been freshly calculated, are listed in Table S1 of SM. The J_2 parameter was obtained from the information of extra spin splitting at the B' site in the B-B' low-energy Hamiltonian, compared to that expected from Stoner I of the B' element and its nominal filling [11]. $t_{B\text{-}B}, t_{B'\text{-}B'}$, and $J_{\rm AS}$ were obtained from a calculation of the corresponding simple perovskite compounds.

Calculated magnetic properties of disordered 3d-4d/5d DPs. The calculated magnetic transition temperatures (T_c) obtained from the ED-MC simulation of the DFT-derived model Hamiltonian, together with the average magnetic moment at the B sublattice (M) with respect to that of the fully ordered compound ($M_{\rm ord}$), is shown in Fig. 3 for all six DPs for a random ASD with a disorder strength of 10%, 37%, and a maximum limit of 50%. The T_c's have been obtained from M vs T plots as presented in Fig. S2 in SM for the representative cases.

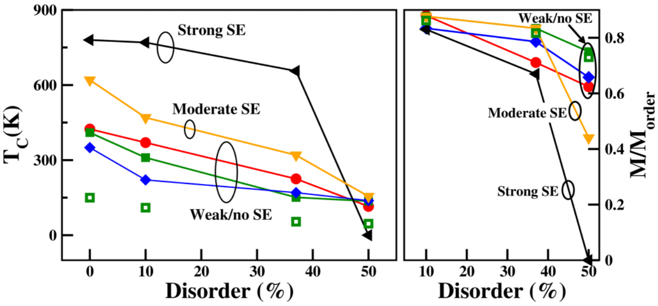

FIG. 3. Variation of T_c (left panel) and $M/M_{\rm ord}$ (right panel) plotted as a function of concentration of random ASD. The data points with a black left triangle, yellow down triangle, red circle, green square, and blue diamond correspond to SCOO, SCReO, SCMO, SCWO, and SFMO, respectively. The green open squares represent data for CCWO.

We observe a distinctly different behavior between DPs exhibiting solely DE-driven magnetism and those having combined DE-SE-driven magnetism. In the case of solely DE-driven compounds such as SFMO, SCWO ($J_2 = 0$), or SCMO having only a weak SE contribution ($J_2 < 0.01$), the ordered magnetic moment is retained to a large extent, showing an about 25%–35% drop from that of the fully ordered compound to the extreme case of 50% disorder, the corresponding drop in magnetic transition temperature being about 60%–70%. Keeping in mind the high transition temperatures of the perfectly ordered compounds with calculated T_c values, e.g., 350 K for SFMO, 410 K for SCWO, and 424 K for SCMO, even the disordering-induced reduced T_c for 50% turns out to be above 100 K. This is markedly different from the expected behavior of SE-driven magnetic systems, for which such a heavily disordered situation will completely suppress the magnetic order. Indeed, the influence of the SE term becomes evident in the magnetic behavior of compounds such as SCOO for which the substantial SE contribution ($J_2 \approx 0.03$) makes the magnetic order completely vanish for the extreme limit of 50% disorder. For SCReO, for which the effect of SE is relatively weaker compared to SCOO ($J_2 \approx 0.02$) though stronger compared to SFMO or SCWO or SCMO, the disordering effect is found to be intermediate between SFMO or SCWO or SCMO and SCOO, with a suppression of the ordered moment by 56% and a suppression of the T_c value by 85% for 50% disorder strength. The Ca counterpart of SCWO, CCWO, shows a similar trend as SCWO, though the corresponding temperatures are suppressed due to a reduction in the B-O-B' bond angle, and a consequent reduction in the hopping interaction.

CrRu puzzle. Having understood the role of disorder on magnetism in a large variety of 3d-4d/5d DPs, and the crucial role of the exchange mechanism, it becomes pertinent to investigate the case of $SrCr_{0.5}Ru_{0.5}O_3$ [6]. The first step towards that will be understanding the driving exchange mechanism in the CrRu system. For this purpose, we carried out a DFT calculation of a hypothetical perfectly ordered double-

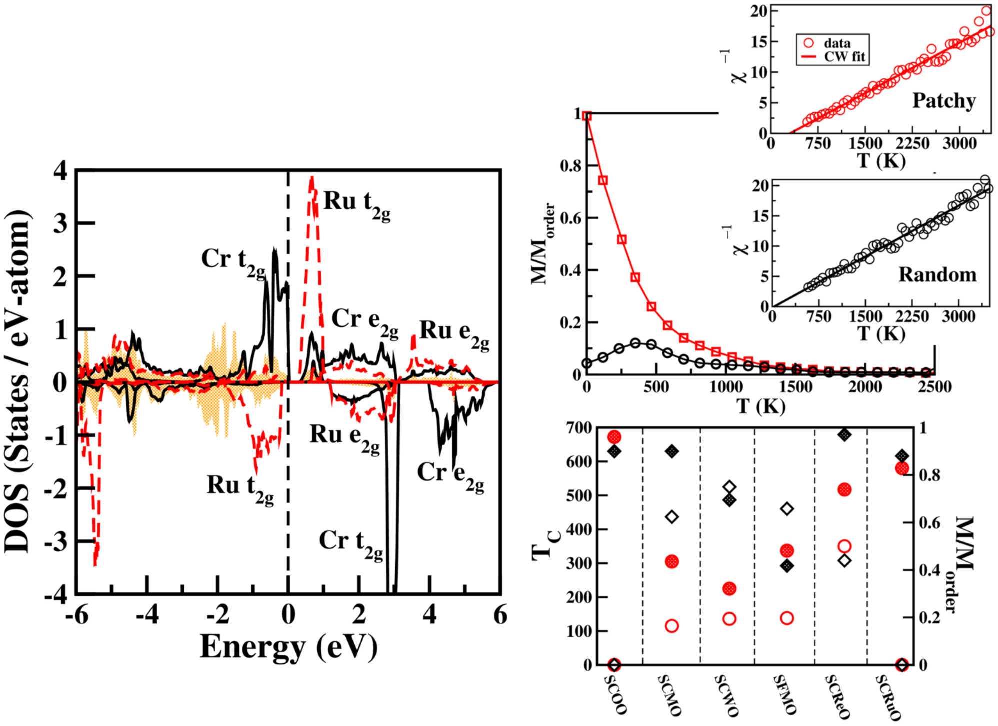

FIG. 4. Left panel: The DFT density of states for the hypothetical fully ordered structure of Sr_2CrRuO_6, projected to Cr d (black solid), Ru d (red dashed) and O p (yellow shaded) states. The zero of the energy is set at Fermi energy. Top right panel: The B-sublattice magnetism plotted as a function of temperature for the fully disordered situation with 50% random ASD (black circles) and for correlated disordered situation with a patchy structure of ordered domains (red squares). The insets show the calculated inverse susceptibility, along with Curie-Weiss (CW) fit. Bottom right panel: Comparison of T_c (red circles) and M/M_{ord} (black diamonds) between the 50% random ASD case (open symbols) and correlated disorder with patchy domain structure (solid symbols).

perovskite counterpart of $SrCr_{0.5}Ru_{0.5}O_3$, i.e., Sr_2CrRuO_6 (SCRuO), with a fully ordered alternating array of Cr and Ru (see SM for details). The DFT calculation [27,28] within the generalized gradient approximation [29] (GGA) with a supplemented Hubbard U (GGA+U) [30] (see SM for choice of U) resulted in an insulating, compensated ferrimagnetic solution (cf. the left panel Fig. 4). The calculated magnetic moments, $2.42\mu_B$ at the Cr site, $-1.65\mu_B$ at the Ru site, and a rather large moment of $-0.11\mu_B$ at the O site, are similar to that obtained for the corresponding isoelectronic compound SCOO [11,31]. The estimated model parameters, presented in Table S1 of SM along with six other naturally occurring DP compounds, show a remarkable similarity with SCOO, suggesting a similar disordering effect on magnetism. Indeed, the consideration of 50% random ASD led to a complete suppression of magnetic order, with the T_c dropping down to 0 K, as found in the case of SCOO. This is, however, in complete contradiction with the observation made in Ref. [6]. It is important to note here that the above conclusions have been drawn based on the assumption that ASD is random. The limited experimental studies [14,15], carried out only for SFMO, suggest the ASD to be correlated, generating a patchy structure, as in the right panel of Fig. 1. Strikingly, the temperature-dependent magnetization at the Cr sublattice of SCRuO is found to be strongly influenced by assuming a correlated disorder instead of a random disorder (cf. the top right panel of Fig. 4). As shown in the insets in the top right panel of Fig. 4, the Curie-Weiss fit to the inverse of high-temperature magnetic susceptibility leads to a 0-K magnetic ordering temperature for random disorder, while the assumption of correlated disorder yields a value of about 370 K, in close agreement with the observed value [6].

We finally checked the influence of correlated ASD for 50% disorder strength in all DPs in this study. Remarkably, we find that the consideration of a patchy structure consisting of ordered domains, separated by APBs, substantially enhances T_c in all cases. The B-sublattice ordered moment also shows a substantial enhancement, especially for cases where magnetism is driven by combined DE and SE. This strongly suggests that in combined DE- and SE-driven magnetic materials such as SCRuO, the cationic order remains preserved to a high degree in a local scale, although the global cationic order gets disrupted due to the presence of APBs separating locally ordered regions. While a global probe such as x-ray or neutron diffraction will be unable to detect any B/B' order signaled by the presence of a superstructure peak, as reported in Ref. [6], local probes such as XAFS [14] or a microscopy study [15] should be able to reveal the presence of such a locally ordered structure. This resolves the apparently puzzling situation of $SrCr_{0.5}Ru_{0.5}O_3$.

In conclusion, our exhaustive study, encompassing a large number of $3d$-$4d$/$5d$ DP compounds, reveals that the influence of the B cation antisite disorder on their magnetic properties, which is unavoidable in any sample, crucially depends on the exchange mechanism. The magnetic behavior is far less susceptible to disorder for DE, while its effect is severe for compounds in which SE becomes operative in addition to DE. Even in the case of compounds, having a SE contribution, the magnetic behavior of the ordered situation may be regained if the disorder is correlated with a high degree of short-range order [14]. This strongly suggests that although the absence of long-range chemical order was reported for CrRu compounds [6], a high degree of short-range order must have been preserved as in the case of SFMO.

Finally, our study does not take into account the effect of oxygen vacancy or excess B/B' [32,33], which needs to be considered separately. As discussed in Refs. [34,35], the oxygen vacancy acts as an effective electron doping, which populates the delocalized electronic state of B and B' in the down spin, thereby causing a shift in the valences of the cations. This is expected to increase the magnetic transition temperature with some reduction in moment [34], as demonstrated in Ref. [18] in the context of La doping of Sr_2FeMoO_6.

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