Nature of "Disorder" in the Ordered Double Perovskite Sr₂FeMoO₆

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The degree of B/B' alternate cation order is known to heavily influence the magnetic properties of $A_2BB'O_6$ double perovskites although the nature of such disorder has never been critically studied. Our detailed x-ray absorption fine structure studies in conjunction with synchrotron radiation x-ray diffraction experiments on polycrystalline Sr₂FeMoO₆ samples with various degrees of disorder reveal that a very high degree of short range order is preserved even in samples with highly reduced long range chemical order. Based on these experimental results and with the help of detailed structural simulations, we are able to model the nature of the disorder in this important class of materials and discuss the consequent implications on its physical properties.

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While the concept of a crystalline solid as a perfect, periodic structure is at the core of our understanding of a wide range of material properties, disorder is in reality ubiquitous, and is capable of influencing various properties drastically. For example, disorder alone can control transport properties, giving rise to a metal-insulator transition at a critical level of disorder [1,2]. In more recent time, there has been substantial increase in interest [3–8] in systems where the simultaneous presence of disorder and strong electron-electron correlation effects, leads to many counter-intuitive results and exciting physics. Most theoretical treatments and experimental interpretations assume uncorrelated distributions of disordered sites, while it is known [9] that physical properties may be strongly influenced by the exact nature of the distribution of disordered sites in a material. The importance of carefully probing the nature of defects as a prerequisite to a proper understanding of complex systems is now well established [10].

The ideal crystal structure of the famous "double perovskite", Sr_2FeMoO_6 , exhibiting large negative magnetoresistance (MR) at high temperatures and low magnetic fields [11], presumes a perfect alternate occupancy of the Fe and Mo ions along the three cube axes, giving rise to the effect of doubling the basic unit perovskite cell. However, the presence of the Fe/Mo disorder, i.e., creation of imperfections by interchanging Fe and Mo ionic positions in a perfectly ordered structure, commonly termed as antisite (AS) defects, is an inevitable reality [12]. Sr_2FeMoO_6 exhibits unique trends both in its magnetic as well as MR behaviors where the degree of this disorder is found to play a critical role [12–14]. Moreover, the electronic structure of Sr_2FeMoO_6 has also been recently shown to get influenced by Fe/Mo cationic disorder [15]. Therefore, eluci-

dating the detailed nature of this cationic disorder is crucial for a microscopic understanding of the unusual properties of this class of materials.

The distribution of AS defects can be illustrated in terms of two limiting scenarios. In one case, they are considered to be placed randomly throughout the lattice [Fig. 1(a)] leading to a homogeneous distribution of defects, often named as AS defects. It is, however, conceivable that the defects may segregate as depicted in Figs. 1(b) and 1(c). It is important to note here that by segregating together, the



FIG. 1 (color online). Slices of 3D models of Fe/Mo cubic lattices (light and dark grey sites representing the Fe and Mo ordered positions, red (blue) sites being Fe (Mo) on the Mo (Fe) sublattice) built (see text) with the same degree of long rang order, S = 0.51, but different kinds of local disorder are shown in panels (a) to (c). (a) random AS distribution: $\xi = \xi_{AS} = 0.63$, (b) small antiphase domains with $\xi = 0.85$ and (c) large antiphase regions with $\xi = 0.99$. (d) (pictorial view): an applied \vec{B}_{ext} aligns neighboring domains while AFM coupling persists in the vicinity of APB defects.

so-called defects recover the perfect periodicity of the original lattice, as shown by the red or blue sites in Figs. 1(b) and 1(c), except that within these patches Fe occupies the nominal Mo site and vice versa. It is reasonable to expect that such ordered patches have properties almost identical as the original ordered lattice [represented by light or dark grey sites in the scheme of Figs. 1(a)-1(c)], since the two lattices are connected by a simple translation. Noting that the properties of Sr₂FeMoO₆ are profoundly affected by disorder [12–14], therefore most reports in the literature implicitly assumed a homogeneous distribution of AS as the appropriate description of disorder in this class of compounds. In contrast, this Letter, establishes the counter-intuitive description of large-scale segregation of the AS forming patches as the correct one. First, we note an apparent conflict between results of synchrotron radiation based x-ray diffraction (XRD) data, suggesting extensive disorder, and x-ray absorption fine structure (XAFS) experiments, indicating nearly perfect ordering, for the same sample disorder. Accurate experiments on several samples with different degrees of disorder, in conjunction with careful simulations of the experimental data, allow us to unify these disparate views establishing that a high degree of short range order in terms of highly ordered domains [Fig. 1(b)], having coherence length of about 1 nm is the only one consistent with the experimental observations for so-called disordered Sr₂FeMoO₆. Using this description, we also discuss the reasons for the drastic influence of this form of disorder on many properties, particularly the magnetic ones, in terms of the boundary between the short patches of ordered structure arising from segregating AS defects and the original ordered lattice, these boundaries being known as the antiphase boundaries (APB) [16].

The detailed synthesis and characterization of polycrystalline Sr_2FeMoO_6 samples with different degrees of disorder (**A**, **B**, **C**, **D**, and **E**) can be found elsewhere [13]. All the experimental data (XRD and XAFS) were collected at the GILDA [17] beam line of ESRF (Grenoble, France). XAFS measurements were performed at the Fe and Mo *K* edges. The analysis of the XAFS data has been performed including single and multiple scattering terms along the lines already described [18]. XRD data were collected using an angle dispersed setup [19] based on a large area detector which allows collecting diffractograms with high statistics suited for revealing weak contributions from superlattice reflections [Fig. 2(a)]. Quantitative XRD patterns analysis was achieved by Rietveld refinement.

The raw XRD patterns are shown in Fig. 2, where the intensity enhancements for (101) and (103) superlattice peaks (shown by \downarrow) with increasing Fe/Mo ordering is clearly observed. The patterns are analyzed by assuming the tetragonal *I*4/*m* space group [20,21], and the main structural results are summarized in Table I. The Mo-O bonds appear systematically shorter than Fe-O in the more



FIG. 2. XRD patterns for all the investigated samples. In the insets: (a) the region corresponding to the (101) superlattice peak for samples A, B and E. (b) the width (FWHM) of lattice (open diamonds) and superlattice (filled diamonds) reflections.

ordered samples and the differences between Fe-O and Mo-O distances decrease with increasing disorder in agreement with literature [20,22]. The *B* and *B'* sublattice fractional occupancy was refined, assuming a random disorder, via the parameter *x* which represents the probability to have Fe or Mo ions on its right sublattices, consequently [23] the long range order (LRO) parameter *S* is calculated as S = 2x - 1 (see Table I).

The k-weighted $(k = \hbar^{-1} \sqrt{2m_e(E - E_0)})$ XAFS spectra $k\chi(k)$, of Fe and Mo K edges for all the investigated samples are presented in Fig. 3 along with their corresponding best fits. It is evident, even from a qualitative insight, that all the spectra (Fe and Mo edges) present very similar features despite the large differences in the LRO obtained from XRD data. In particular, the Fourier transforms (FT) of Mo K edge $k\chi(k)$ [Fig. 3(d)] show that the effects of LRO are weak and they only slightly modify the FT features in the region around 3.8–4 Å. These findings suggest that a high degree of local order is always present in our samples despite the observed large differences of LRO. The main structural parameters obtained from quantitative XAFS analysis, are presented in Table II. From the XAFS data it is possible to quantify the degree of short range order (SRO) $\alpha = 2\xi - 1$ [23] by directly measuring the probability ξ to find locally ordered configurations around the absorber [24]. In case of a random distribution of defects the probability to find ordered configurations Fe-O-Mo should be $\xi_{AS} = x^2 + (1 - x)^2$, which results in $\xi_{AS} = (1 + S^2)/2$ (Table I). XAFS results demonstrate that the local order around Fe and Mo varies to some extent with changing the LRO, but clearly the variation of ξ (Table II) is much smaller than expected for a random distribution of AS defects. Therefore these experimental results can clearly refute the scenario depicted in Fig. 1(a) and the XAFS data unambiguously establishes that the local structure around Fe and Mo preserves a high degree

TABLE I.	Left column reports the crystallographic order parameter S, the crystallographic structure and the ξ_{AS} (see text) calculated
in the case of	f random defect distribution. On the right columns ξ_D is the probability of ordered Fe-O-Mo configurations calculated in a
3D lattice r	odel with antiphase ordered domains of average size \overline{D} (in lattice unit: $l = a/\sqrt{2}$ is the perovskite cube edge).

Sample	S	a = b (Å)	<i>c</i> (Å)	Fe-O ₁ (Å)	Fe-O ₂ (Å)	Mo-O ₁ (Å)	Mo-O ₂ (Å)	$\xi_{\rm AS} = (1 + S^2)/2$	ξ_D	$\bar{D}\left(l ight)$	$\Delta D(l)$
А	0.96(4)	5.572(4)	7.888(5)	2.05(5)	2.01(4)	1.89(4)	1.94(4)	0.96(4)	0.97	2.0	0.6
В	0.81(8)	5.574(4)	7.889(4)	2.03(5)	2.00(5)	1.92(5)	1.96(5)	0.82(7)	0.92	2.8	0.9
С	0.51(3)	5.571(3)	7.892(4)	1.99(4)	1.99(4)	1.96(4)	1.95(4)	0.63(2)	0.85	3.2	0.9
D	0.33(6)	5.573(3)	7.901(3)	1.98(5)	1.97(4)	1.98(5)	1.98(5)	0.55(3)	0.80	3.0	0.9
Е	0.18(6)	5.572(4)	7.895(4)	1.98(5)	1.97(4)	1.97(4)	1.98(4)	0.52(3)	0.78	3.2	0.8

of cation order, with Fe-O-Mo configurations along the perovskite cube edge, always preferred over a random cation distribution [25].

Now, we carefully reexamine the bulk XRD patterns, especially the 2θ regions close to the order related reflections. It is found that the superlattice peaks invariably possess significantly larger width compared to the basic lattice related peaks [Fig. 2(b)], which indicates a reduction in the coherence length of the ordered domains. Moreover, these superlattice peaks get systematically wider with increasing disorder, while the widths of the lattice related peaks remains nearly unchanged [Fig. 2(b)]. These observations indicate that the model presented in Fig. 1(b) is



FIG. 3. XAFS results. (a),(b) experimental (dots) and best fit (full lines) for all samples/edges investigated. (c) modulus and imaginary part of FT from Fe *K*-edge XAFS data of the sample D (dots), the best fit obtained refining the local order parameter ξ (upper curves) and fixing it to the value given by XRD (lower curves) are shown for sake of comparison. (d) |FT| of *k*-weighted experimental (dots) and best fit (full lines) XAFS data at the Mo *K* edge.

most appropriate for Sr_2FeMoO_6 , where the decreasing of LRO progressively raises the presence of AS patches, so reducing the coherence length of the ordered regions and broadening the order related peaks.

To further verify the effect of the presence of antiphase regions on LRO and SRO, and to visualize the effect of different kinds of disorder on the diffraction patterns, we built a 3D model of a cubic lattice in which two B-site ions are arranged on two different sublattices. Now, for a given value of LRO parameter S (according to XRD data), different kind of AS defects are applied [Figs. 1(a)-1(c)]: randomly distributed or organized in antiphase regions with average diameter \overline{D} and uniform distribution of D in between $\overline{D} \pm \Delta D$. The values of \overline{D} and ΔD are refined (Table I) in order to fit ξ_D to the experimental XAFS values ξ . The results obtained suggest that the antiphase domains have a dimension of 8-13 Å and their sizes decrease with increasing S. As shown in Fig. 4, the effect of SRO remains invisible in XRD patterns as it becomes appreciable only at logarithmic scale for noiseless data.

The above mentioned differences in the distributions of cationic disorders in Sr_2FeMoO_6 is also expected to affect the magnetic behavior of the system significantly. Recently, it has been shown that the magnetic domain walls are mostly pinned to the antiphase boundaries [26] where the domain walls extend by few atoms to both sides of the

TABLE II. Results of the XAFS data analysis at Fe and Mo *K* edges.

Fe K edge										
Sample	$\xi(Fe)$	$R_{\rm FeO}$ (Å)	$R_{\rm FeSr}$ (Å)	$R_{\text{Fe-Mo}}$ (Å)	$R_{\text{Fe-Fe}}$ (Å)					
А	0.91(5)	1.996(8)	3.48(4)	3.93(5)	3.97(6)					
В	0.96(2)	1.989(5)	3.47(3)	3.94(3)	3.96(5)					
С	0.87(7)	1.979(8)	3.46(4)	3.93(3)	3.95(5)					
D	0.83(6)	1.988(5)	3.47(3)	3.94(4)	3.89(6)					
Е	0.77(7)	1.978(1)	3.47(4)	3.94(3)	3.89(5)					
Mo K edge										
Sample	$\xi(Mo)$	$R_{\rm MoO}$ (Å)	R_{MoSr} (Å)	$R_{\text{Mo-Fe}}$ (Å)	$R_{\text{Mo-Mo}}$ (Å)					
А	0.97(5)	1.944(8)	3.42(1)	3.94(2)	3.89(2)					
В	0.92(2)	1.944(8)	3.43(1)	3.95(2)	3.88(2)					
С	0.85(4)	1.943(9)	3.43(1)	3.94(2)	3.88(2)					
D	0.70(5)	1.937(8)	3.42(1)	3.94(2)	3.87(2)					
Е	0.72(3)	1.936(9)	3.43(1)	3.93(2)	3.87(2)					



FIG. 4 (color online). Left: the calculated SL peak intensity for the two cases with the same LRO S = 0.51, but different kinds of defects [see Figs. 1(a) and 1(b)]. The superlattice peak calculated for the S = 1 case is also shown for sake of comparison. Right: the same data plotted in semilog scale, the weak effect due to different kinds of local order can be put in evidence.

particular point defect [27]. For fewer number of APBs, i.e., extended sizes of the antiphase domains, it should be easier to achieve large magnetic moments by aligning neighboring domains across APB [see the description in Fig. 1(d)] with the help of external magnetic fields. While such spin alignments are likely to become progressively difficult for smaller domains and therefore, only a part of the total expected ferromagnetic moment can be realized. Consistent with the present results, previous magnetic studies as a function of disorder [13,14] strongly suggest that the presence of multiple nanosized antiphase domains is more likely than highly extended domains with relatively fewer number of antiphase boundaries.

The nature of structural disorder is expected to play a crucial role in the physical response of every complex system. Combining complementary probes and theoretical modeling, it is possible to achieve an accurate description of defects at different length scales. Our XAFS studies of local order in Sr₂FeMoO₆ demonstrate that a high degree of cation order is preserved locally even in samples with high degree of long range disorder. This indicates that the formation of APB patches is favored compared to homogeneous distribution of AS defects. The short and long range order features in Sr₂FeMoO₆ can be understood in terms of locally ordered regions. Our analysis of the diffraction data, with the help of simulations, establishes the presence of nanosized antiphase domains in the system which profoundly influence magnetic properties of this interesting material. We note that there is an ample variety of compounds within the double perovskite family which are being vigorously investigated for their interesting physical properties, particularly magnetism, by a large number of groups around the world and in all these systems the "ordering" plays an important role. It is obvious that our results here represent an important step in understanding the properties of such materials.

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- [24] This probability is evaluated by the ratio $\xi = N_{\text{FeMo}}/N_{\text{Fe}}$ (= $N_{\text{MoFe}}/N_{\text{Mo}}$), in which the number of ordered configurations Fe-O-Mo along the perovskite cube edge N_{FeMo} (N_{MoFe}) is measured by XAFS, and the total coordination number of the absorber is $N_{\text{Fe}} = N_{\text{Mo}} = 6$.
- [25] In order to confirm our finding and highlight the sensitivity of XAFS to different local orderings, we present in Fig. 3(c) the results of fitting of Fe *K*-edge data either by refining ξ , or by imposing $\xi = \xi_{AS}$ as expected for a random AS defect distribution. It is evident that the random model, based on XRD results, fails to fit the XAFS data giving large discrepancies in the refinement.
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