



The story of 'ordering' in highly 'disordered' double perovskites

Sugata Ray

Department of Materials Science

Indian Association for the Cultivation of Science

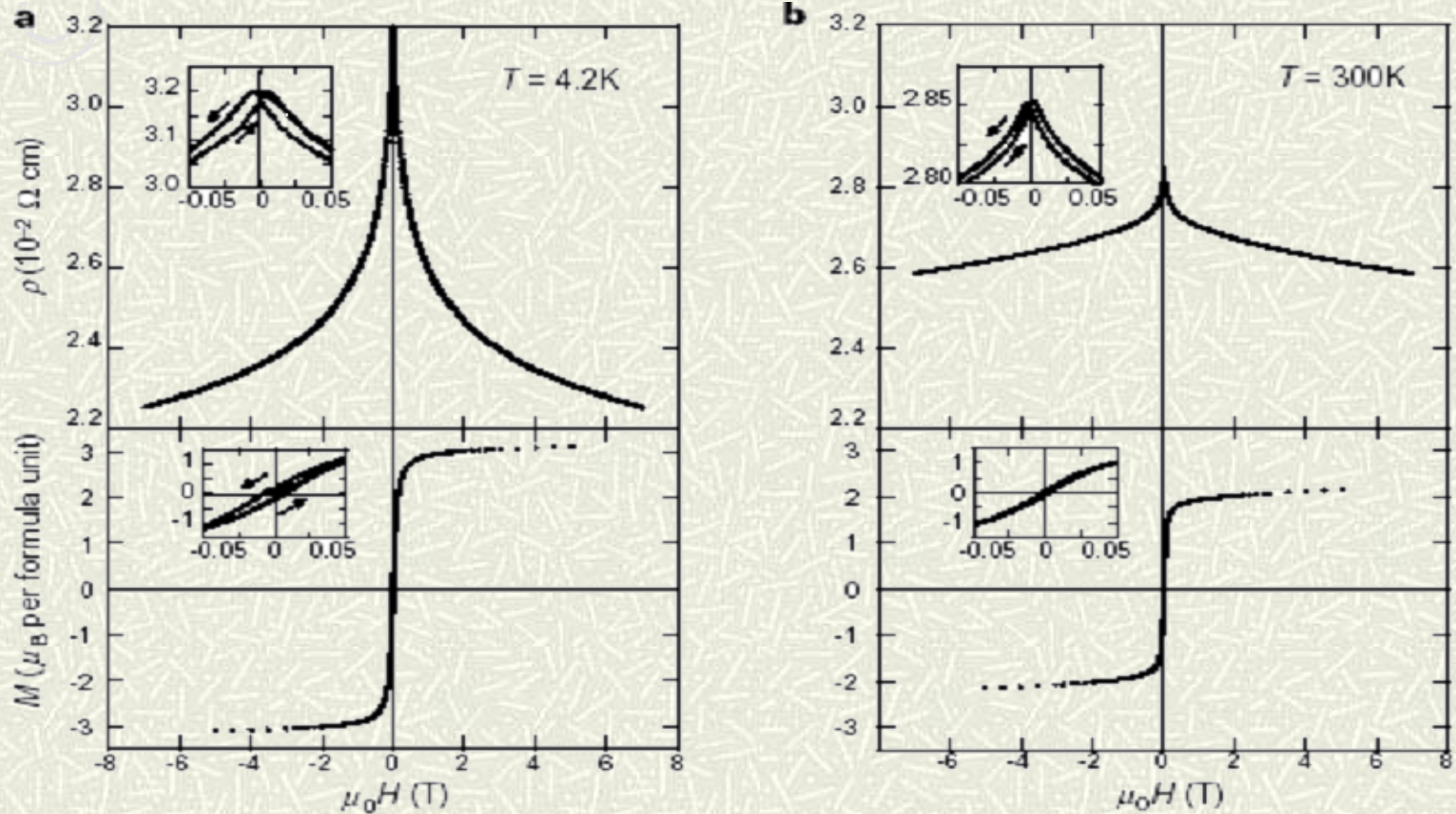
**MAGNETISM, SUPERCONDUCTIVITY AND PHASE
TRANSITIONS IN NOVEL AND COMPLEX MATERIALS**

11th – 14th November, 2009

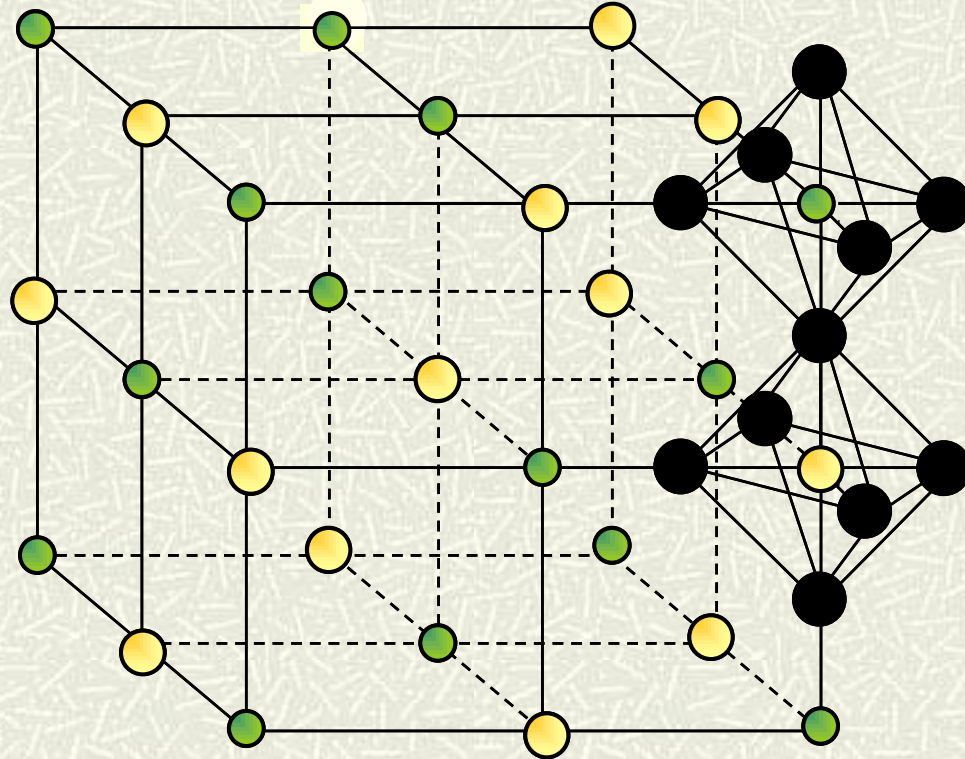
- ❖ **C. Meneghini**
- ❖ **D. D. Sarma**
- ❖ **F. Liscio**
- ❖ **F. Bardelli**
- ❖ **S. Mobilo**



Room temperature Tunneling Magnetoresistance (TMR) in double perovskite $\text{Sr}_2\text{FeMoO}_6$

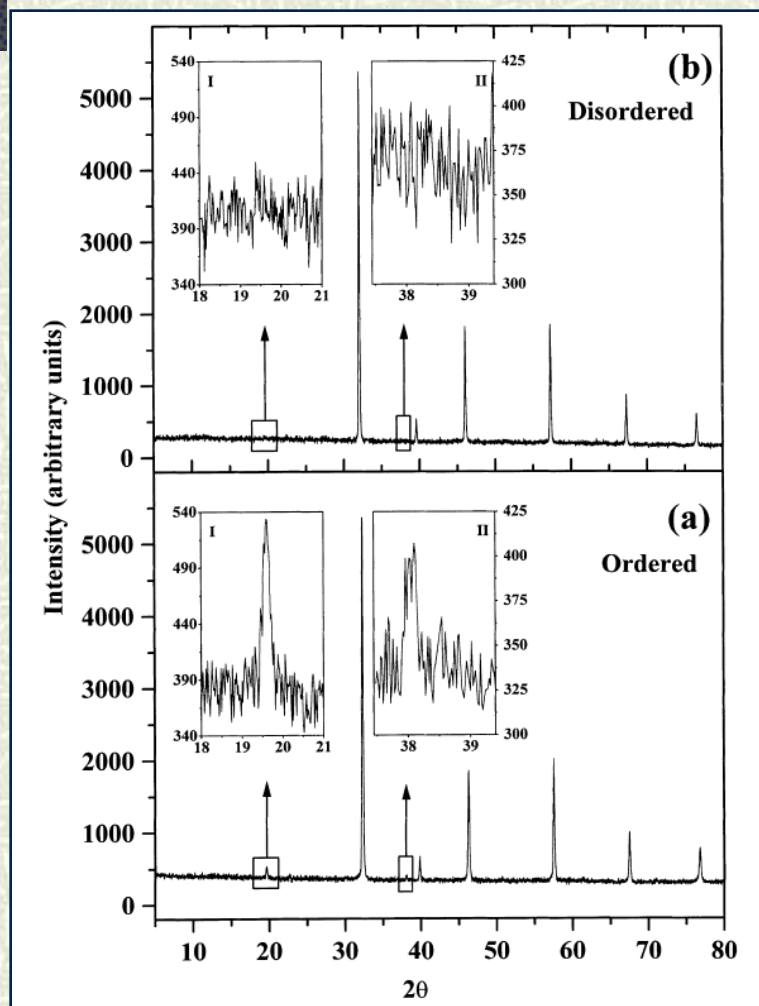


The inevitable disorder



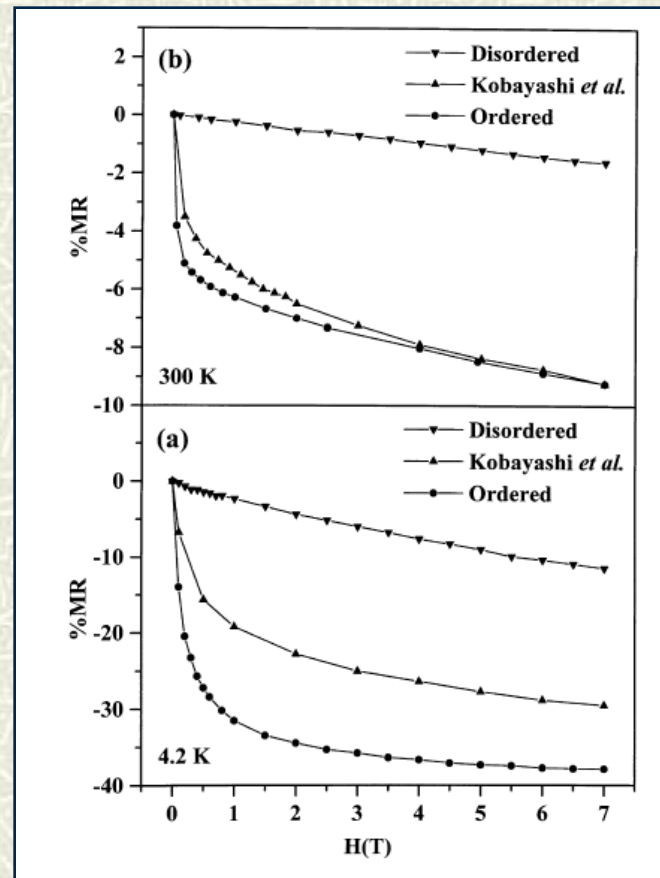
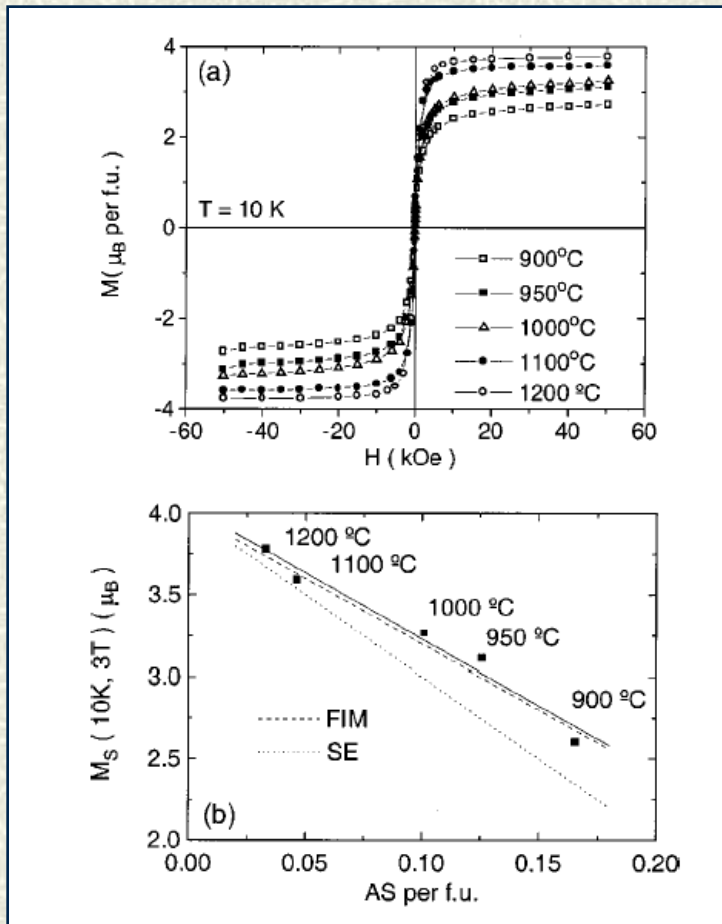
**Cationic disorder is an
integral part of
 $\text{Sr}_2\text{FeMoO}_6$ structure**

Experimental tool to probe disorder



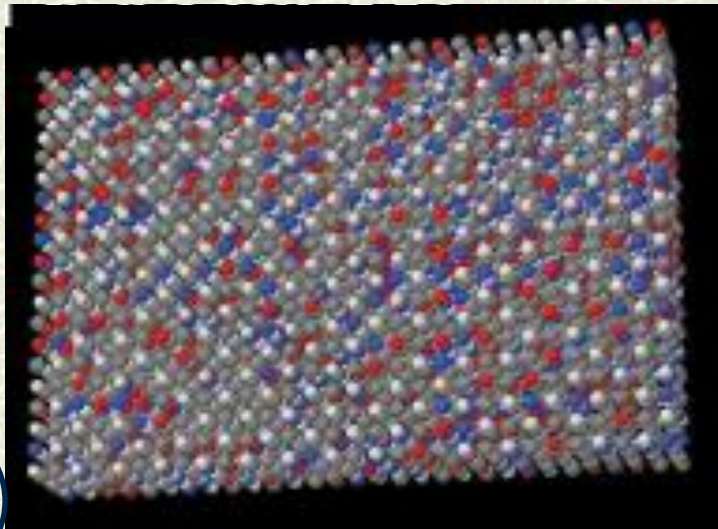
The intensity variations of these order-related peaks provide us an estimate of the anti-site disorder but does not offer any clue about their physical distribution in the system.

The implications of disorder



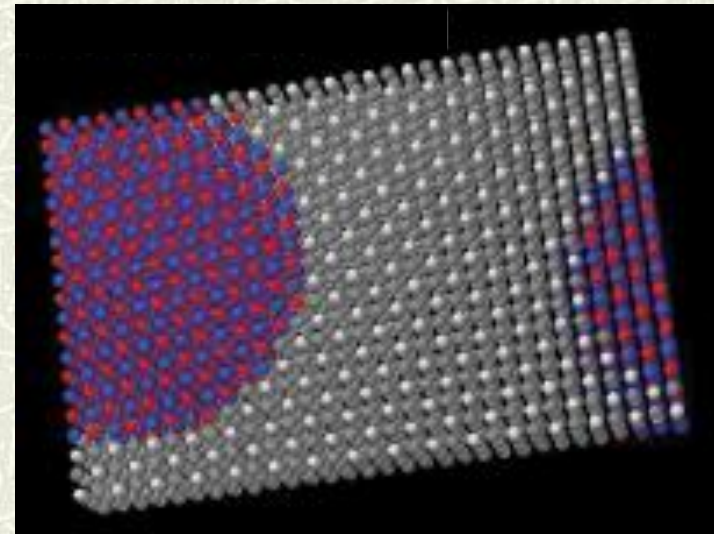
Solid State Commun. 114, 464 (2000)

But, how is the disorder really?



A

Light Grey : Fe at the Fe-site
Dark Grey: Mo at the Mo-site
Red: Fe at the Mo-site
Blue: Mo at the Fe-site



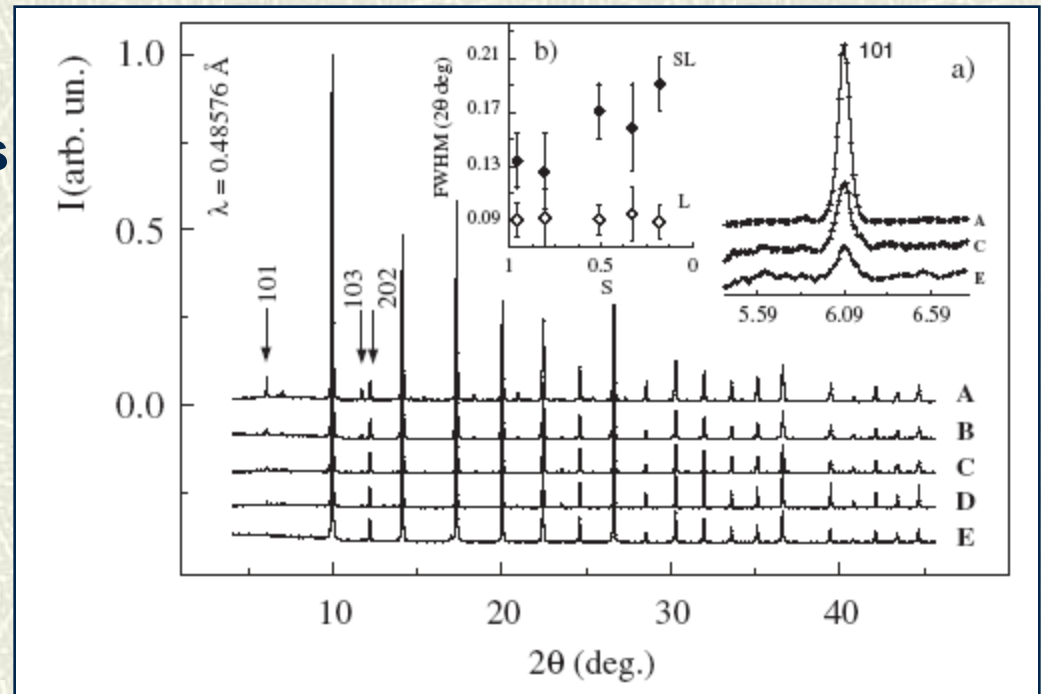
B

Similar number of anti-sites here but very few Fe-Fe or Mo-Mo nearest neighbour connectivities (APB). So, will the bulk properties differ in this case?

We decide to probe this

A set of pure $\text{Sr}_2\text{FeMoO}_6$ samples with various degrees of Fe/Mo antisite disorder were synthesized.

An unique melt-quenching method to produce highly disordered sample proved to be extremely helpful in this matter.



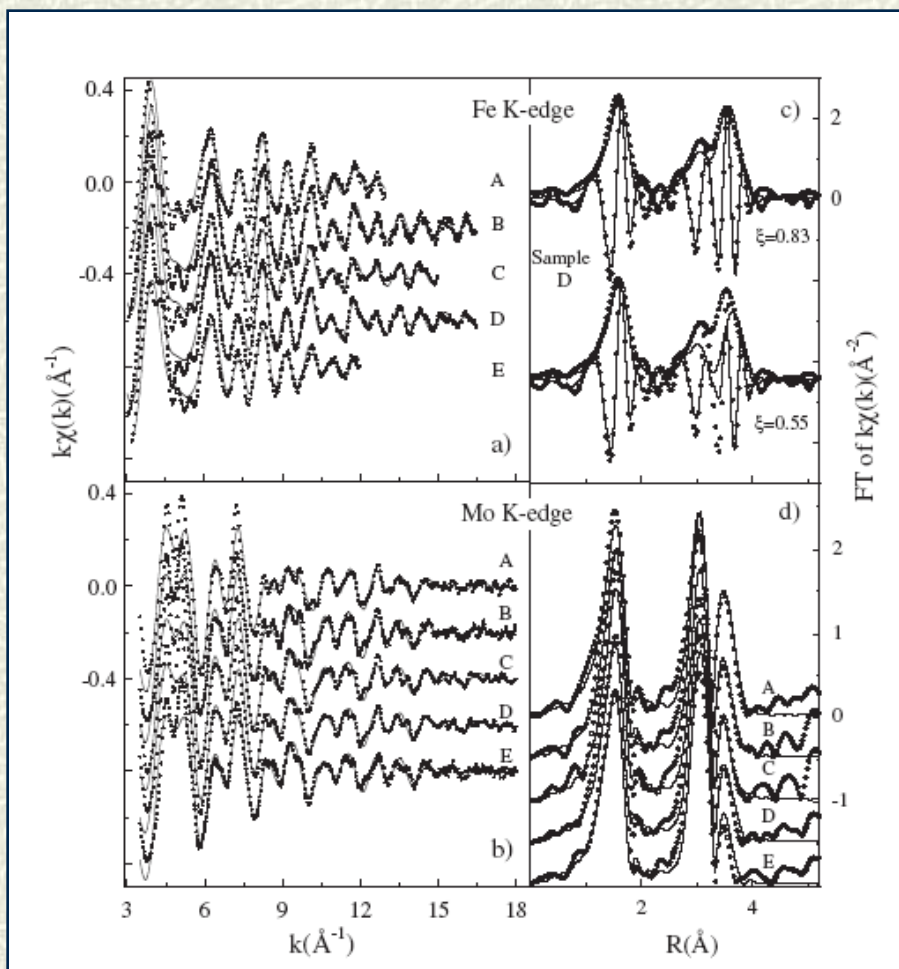
The B and B' sublattice fractional occupancy was refined, assuming model A, via the parameter x which represents the probability to have Fe or Mo ions on its right sublattices, consequently the long range order (LRO) parameter S is calculated as $S = 2x - 1$.



What refinement tells us

Sample	S	$a = b$ (Å)	c (Å)	Fe-O ₁ (Å)	Fe-O ₂ (Å)	Mo-O ₁ (Å)	Mo-O ₂ (Å)
A	0.96(4)	5.572(4)	7.888(5)	2.05(5)	2.01(4)	1.89(4)	1.94(4)
B	0.81(8)	5.574(4)	7.889(4)	2.03(5)	2.00(5)	1.92(5)	1.96(5)
C	0.51(3)	5.571(3)	7.892(4)	1.99(4)	1.99(4)	1.96(4)	1.95(4)
D	0.33(6)	5.573(3)	7.901(3)	1.98(5)	1.97(4)	1.98(5)	1.98(5)
E	0.18(6)	5.572(4)	7.895(4)	1.98(5)	1.97(4)	1.97(4)	1.98(4)

Can we see the situation inside?



The k-weighted XAFS spectra of Fe and Mo K edges for all the investigated samples are shown here, 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 [Fig. (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.



Quantitative results

From the XAFS data it is possible to quantify the degree of short range order (SRO) $\alpha = 2\xi - 1$ by directly measuring the probability to find locally ordered configurations around the absorber. 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 $\xi_{AS} = (1 + S^2)/2$, which should be

Sample	$\xi_{AS} = (1 + S^2)/2$
A	0.96(4)
B	0.82(7)
C	0.63(2)
D	0.55(3)
E	0.52(3)

But, what we found from the experiments are,

Fe K edge					
Sample	$\xi(\text{Fe})$	$R_{\text{FeO}} (\text{\AA})$	$R_{\text{FeSr}} (\text{\AA})$	$R_{\text{Fe-Mo}} (\text{\AA})$	$R_{\text{Fe-Fe}} (\text{\AA})$
A	0.91(5)	1.996(8)	3.48(4)	3.93(5)	3.97(6)
B	0.96(2)	1.989(5)	3.47(3)	3.94(3)	3.96(5)
C	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)
E	0.77(7)	1.978(1)	3.47(4)	3.94(3)	3.89(5)
Mo K edge					
Sample	$\xi(\text{Mo})$	$R_{\text{MoO}} (\text{\AA})$	$R_{\text{MoSr}} (\text{\AA})$	$R_{\text{Mo-Fe}} (\text{\AA})$	$R_{\text{Mo-Mo}} (\text{\AA})$
A	0.97(5)	1.944(8)	3.42(1)	3.94(2)	3.89(2)
B	0.92(2)	1.944(8)	3.43(1)	3.95(2)	3.88(2)
C	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)
E	0.72(3)	1.936(9)	3.43(1)	3.93(2)	3.87(2)



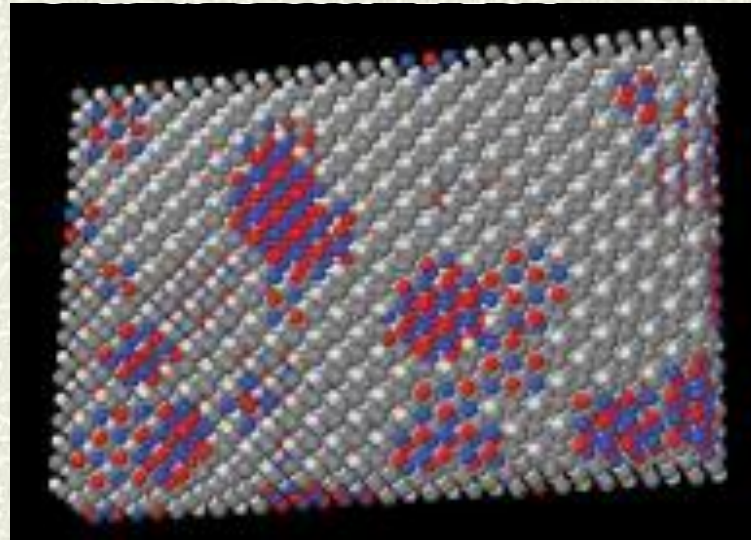
What do these results tell us?

May be we conclude that model B is the correct model to be accepted? But the problems with such an assumption are,

- **The properties vary strongly with increasing LRO**
- **The experimental ξ is not expected to change so much if model B is true.**
- **How do we explain the changes in the FWHM of the superlattice peak?**

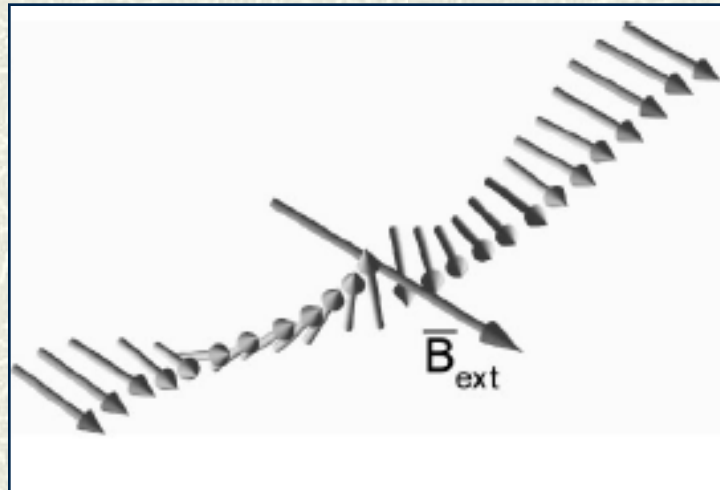


So, the true scenario is....



The system has many small anti-phase domains (of order of 1-2 nm), which are perfectly ordered within itself but are separated from the rest of the parts by anti-phase boundaries (APB). Such a situation demands presence of many APB's, consistent with the experimental ξ value and it also explains the broadening effect of the superlattice peaks.

How about the property variation?



It has been experimentally shown that magnetic domain walls are usually pinned with the anti-phase boundaries and the structure of the magnetic domain walls take a shape close to the one shown above.

Therefore, it is a likely possibility that presence of nanodomains makes the magnetic domain walls strained which in turn opposes magnetic alignment along the applied field and consequently, weaker moment.



Conclusion

1. Our work reveals that the whole understanding of site-disorder in the double perovskites needed more detailed understanding.
2. It also appears that the true nature of chemical disorder in any system, in general, should be checked more carefully, in order to connect them with the observed property changes.

Phys. Rev. Lett. 103, 046403 (2009)



Thank you