

Some very recent neutron diffraction studies (E. E. Rodriguez, Th. Proffen, A. Llobet, J. J. Rhyne & J. F. Mitchell, manuscript in preparation) lend additional support for this new model. Using combined Rietveld and pair distribution function analyses, the neutron work extracts the most detailed map to date of the atomic positions in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. In addition to providing convincing support for the CE structure (although with much smaller charge alterations on the Mn ions than the naïve $3+/4+$ picture), it confirms an earlier suggestion that distortions of the oxygen octahedra occur around the formally $4+$ Mn ions⁹. These distortions create local dipole moments. In $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, adjacent dipole moments point in opposite directions so there is no overall electric polarization. However, for compositions away from 50% CaMnO_3 , complete cancellation should not be expected, and a net polarization could result.

Unfortunately, these proposed charge-ordered multiferroics are unlikely to be of immediate practical use in terms of device applications. The electric polarization is predicted to be very small and the magnetic ordering is essentially antiferromagnetic. Also, the electric and magnetic ordering temperatures of the proposed systems will probably be far below room temperature. Nonetheless, such an alternative route to ferroelectricity, which is necessarily strongly interwoven with the associated magnetic ordering, is a very exciting concept that will surely stimulate further research towards practical magnetoelectric multiferroics.

References

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MATERIAL WITNESS

Watching paint dry

“As a picture ages, and the paint dries out — it takes about fifty years — it cracks in a certain pattern. What we call the craquelure.” In Robertson Davies’ novel *What’s Bred In The Bone*, Francis Cornish is learning the fine points of art forgery from an expert named Saraceni. They place anonymous old portraits, freshly repainted to show grander (and more valuable) subjects, into a furnace. “After about fifteen minutes of slow baking they emerged with, sure enough, tiny hairlines that satisfied the Meister.”



Saraceni knew his business. Some forgers have been considerably less sophisticated; they have even been known to paint on a fine web of craquelure by hand — a deception that might fool the eye of a careless buyer but which would be immediately obvious under a magnifying glass.

Craquelure is a subtle fingerprint of authenticity. Its precise structure may vary according to where the picture was painted — there are French, Italian, Dutch and Flemish ‘styles’ of craquelure. And it provides a record of the treatment the painting has received over the course of its lifetime: the handling, transportation and changes in ambient environment.

This web of cracks provides a non-destructive means of analysing the artist’s materials and techniques. The features of the pattern can reveal the nature of the support (canvas or wood) and of the white undercoat or ‘ground’ (typically gypsum or chalk, bound with glue or oil). For example, many late-medieval altarpieces were painted on poplar, an unstable wood prone to shrinkage or swelling. That’s why a lot of effort has gone into developing methods for digitally scanning paintings to classify the craquelure pattern.

It’s of paramount importance, then, to know how cracking of paint surfaces happens in the first place. Although poor handling can wreak havoc — Titian’s *Bacchus and Ariadne* was twice removed from its wooden support and rolled up — craquelure is also an unavoidable consequence of the slow drying of paint. So a paper by Wai Peng Lee and Alexander Routh (*Langmuir* **20**, 9885; 2004) which posits a new mechanism for cracking in thin films ought to be of considerable interest to art conservators and historians.

The standard idea is that, as the film dries and contracts, the spacing of cracks is determined by a balance between the elastic energy released and the cost of rupturing the film and creating new surfaces. This suggests that the average size of the fragments is proportional to the film thickness. But Lee and Routh present evidence that cracking may instead have a hydrodynamic origin, governed by the capillary pressure set up due to depletion of the solvent at the drying front.

This introduces a new length-scale to the crack spacing, which has specific power-law relationships to the film thickness t (varying as $t^{0.8}$), the evaporation rate and the size of the particles in the film (the pigment particles in paint, say). The ‘signature’ of craquelure — the characteristic size of the cracks — might then encode revealing aspects of the painter’s technique, such as how thinly he mixed his paints or how the works were stored as they dried.

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