Achievements in Research – Paolo G. Radaelli

Over his 27-years career, Paolo G. Radaelli (PGR) made seminal contributions to the physics of transition metal oxides and related compounds, using neutron and X-ray scattering and spectroscopy as primary tools. In the past three years, he opened up new field of research in **photo-induced magnetism** and **real-space antiferromagnetic topology**. His name is most clearly associated with bodies of work on **manganites** and **multiferroics**, with textbook discoveries on **charge and orbital ordering**, **phase separation**, and the **exchange-striction** and **ferroaxial** mechanisms of multiferroicity. His early **structural studies of high-T_c superconductors** and work on **phase transitions in frustrated systems** include seminal publications. PGR's **methodological contributions**, both experimental and theoretical, paved the way for much recent research. PGR led the structural condensed matter physics component of the work, including the experiments and the development of models for the structure/property relations, whilst collaborating with beamline scientists (e.g., D.E. Cox, A. Bombardi) and junior colleagues (e.g., L. Chapon, R.D. Johnson). Samples were usually grown and characterised by others, such as D. Hinks (Argonne) and S.-W. Cheong (Bell Labs and later Rutgers), but for the most recent papers most measurements were performed in PGR's group in Oxford.

Real-space antiferromagnetic topology and photo-induced magnetism

In the last 3 years, PGR opened up *two new important research fields*. Magnetic 'particles' with topological properties in real space (e.g. skyrmions) are of great fundamental significance and could enable entirely novel spintronics applications. Antiferromagnetic (AFM) analogues would have many advantages in terms of speed and control, and have been much sought after. Using a mapping version of photo-electron emission microscopy (X-PEEM) developed in his group, PGR discovered a network of *vortices and antivortices* in the *AFM* domain structure of α-Fe_2O_3, which are strongly coupled to metallic overlayers (**Ref 205**, 18 cit.). Later, he discovered that AFM *merons/antimerons/bimerons* can be generated at will in the same system (**Ref 217**).

The ability to control magnetism by light has been a longstanding dream, which could lead to a new generation of ultrafast light-driven switches. Prompted by a collaboration with MPSD-Hamburg, PGR used group-theoretical techniques to predict the existence of *photo-ferroicity* (*light-induced multi-ferroicity*) in several classes of materials (**Ref 203**). This phenomenon, quite distinct from the Faraday effect, was also confirmed experimentally by PGR and collaborators (**Ref 213**).

Multiferroics

PGR's most original and significant research legacy has been in the fields of multiferroics, thanks in large part to the research tools he had previously developed. As a scientist and group, PGR had transformed the capabilities of the ISIS neutron source for magnetic powder and single crystal diffraction, raising these techniques from a few demonstration experiments to becoming among the most productive at ISIS. The Diamond synchrotron, which began operation in 2007, had outstanding facilities for magnetic X-ray diffraction, and PGR was among the first and most engaged users, particularly in the development of data analysis. The "renaissance" of multiferroic research, started by a paper by T. Kimura, *et al.*, *Nature* 426, 55 – 2003, was an exciting time to deploy these techniques, which are ideal to study the complex multiferroic magnetic structures.

Multiferroics are materials in which the electrical polarisation P is associated with or induced by magnetic ordering. Early on, most of the community focussed on the so-called *cycloidal magnets*, in which P is induced by antisymmetric exchange interactions in a rotating magnetic structure. In **Ref 128** (cited 276 times), PGR demonstrated for the first time that electrical polarisation can occur in a *collinear* magnetic structure via *exchange striction,* associated with the much stronger Heisenberg (symmetric) exchange interaction, and showed that exchange striction underpins ferroelectricity in the $RE\mathrm{Mn_2O_5}$ (RE= Y, Bi or rare earth) family of compounds. After some initial scepticism, this idea has been fully corroborated, and several other unrelated materials in the same class have been found. More recently, PGR proposed another, completely different mechanism for generating electrical polarisation upon magnetic ordering, which he named *ferroaxial coupling.* Unlike cycloidal multiferroics, ferroaxial multiferroics are magnetically *chiral*, and electrical polarisation is generated by coupling to crystal structures with certain symmetries. PGR and his group discovered several ferroaxial multiferroics, including $Cu_3Nb_2O_8$ and $CaMn_7O_{12}$ (**Ref 171**, 183 cit.), which has the largest knoen magnetically induced polarisation measured to date at a relatively high temperature (90 K). More recently, PGR and his group have proven that the helical magnetic structure in $CaMn_7O_{12}$ is coupled to incommensurate orbital ordering through "magneto-orbital helices" (**Ref 176**, 64 cit.), a novel type of texture that is distantly related to that of $La_{0.5}Ca_{0.5}MnO_3$ (**Ref 88**, 809 cit.).

The functionality of many magnetic and multiferroic materials is strongly dependent on the behaviour of their magnetic domains. In **Ref. 157** (43 cit.), PGR pioneered the use of *neutron spherical polarimetry* to measure the multiferroics domain population as a function of applied *electric* field, and measured a complete ferroelectric hysteresis loop through the neutron polarisation matrix elements. In later papers, circularly polarised X-ray diffraction and X-PEEM were employed to provide comparable information on much smaller length-scales (down to ~10 nm). This work inspired a very significant change in direction of PGR's research, which now focuses on *films and prototype devices at room temperature*. Using X-PEEM, PGR and collaborators imaged epitaxial films of $BiFeO_3$ at room temperature, demonstrating the presence of a sub-micron domain texture (**Ref 195**, 14 cit.), and later demonstrated electric field control and coupling to a ferromagnetic over-layer – an important step towards multiferroic devices.

Geometrically frustrated systems and the water ice

Starting from the early 2000's, PGR made a decisive contribution to the understanding of the electronic/magnetic properties of geometrically frustrated oxides. Early studies of complex physics in oxides date back to the pre-war period, most famously the work of Verwey on the metal-insulator (MI) transition in magnetite (E. J. W. Verwey, *Nature (London)* 144, 327 – 1939). In the 1950's, there was a renewed interest, both theoretical (e.g., P. W. Anderson, *Phys. Rev.* 102, 1008 – 1956) and experimental (F. J. Morin, *Phys. Rev. Lett.* 3, 34 – 1959). One hugely important class, of which the VO_2 is the best-known example, are materials in which a gap opens in the magnetic excitations, leading to a diamagnetic state. The exact cause of these transitions is still actively debated, but in the early 2000's they were believed to be the magnetic analogues of charge density waves (whence the collective name of spin-Peierls transitions), driven by Fermi surface instabilities, and generally restricted to 1-D systems. The work by PGR on $CuIr_2S_4$ (**Ref 119**, 253 cit.), carried out by a combination of synchrotron and neutron powder diffraction/PDF, was both unexpected and influential, because it established that this phenomenon could occur in three-dimensional (cubic) materials. PGR found that the underlying microscopic mechanism is only distantly related to Peierls transitions. In fact, a complex low-temperature distortion pattern around the Ir atoms leads to *charge ordering* and the formation of *metal-metal bonds*. $MgTi_2O_4$ (**Ref 126**, 141 cit.) has closely related phenomenology but an altogether different "helical" geometry.

In collaboration with the group of J.P. Attfield, PGR revisited Fe_3O_4 (magnetite), arguably the ancestor of all these materials. Verwey had long ago speculated that Fe2+ and Fe3+ charge ordering may drive the MI transition at 120 K, but no convincing structural model had yet been proposed. In the seminal **Ref 118** (249 cit.), the first stable model of the Fe_3O_4 charge-ordered structure was refined by a combination of X-ray and neutron data. Although later further refined by single-crystal data, this model remains a cornerstone of contemporary Fe_3O_4 research.

The model in **Ref 118** does not obey the so-called Anderson condition, which is the charge equivalent of the Bernal-Fowler ("two-in-two-out") rule for water ice. The fascinating analogy between spinel oxides and water ices (which are closely related structurally) was later pursued by PGR in collaboration with C.G. Salzman and others. Twelve water ice phases were then known, often distinguished by subtle differences in the proton ordering, indicative of a complex low-energy landscape that is characteristic of frustrated geometries. In a series of landmark experiments, PGR and collaborators discovered three new phases of water ice, ice XIII, XIV (**Ref 140**, 172 cit.) and later XV, and refined their crystal structures by neutron powder diffraction.

Colossal magnetoresistance manganites

PGR developed key elements of understanding of this important class of materials, and his lasting legacy is in the bedrock of modern research. In the early nineties, R. von Helmholt *et al.* (*Phys. Rev. Lett.* 71, 2331 ~1993) and S. Jin *et al.* (*Science* 264, 413 ~1994) "re-discovered" that certain manganese oxides with the perovskite structure possessed very large low-temperature magnetoresistances. Although evidence of this existed since the 1950's, these papers in effect started the field of Colossal Magnetoresistance (CMR), which was to dominate condensed matter physics for the next decade. CMR manganites have general formula $A_{1-x}A'_xMnO_3$, where *A* is a 3-valent element (typically, La, Y or a rare earth), and *A'* is a divalent elements (Sr, Ba, Ca). In the early days of CMR, it was natural to emphasise the fact that by varying *x* one varies the Mn^{3+}/Mn^{4+} ratio, because the concept of doping had become very familiar to people from the related field of high-T_c superconductivity. It is perhaps for this reason that **Ref 63**, a relative simple paper on structure-property relations in collaboration with the Bell Labs group, has been so influential in the field, and remains PGR's most cited work (1,886 cit.). **Ref 63** makes the following point, backed by high-quality magneto-transport and powder neutron diffraction data: the temperature-doping phase diagram $A_{1-x}A'_xMnO_3$ is completely different for different *sizes* of the *A*/*A'* site, the key additional parameter being the *Goldschmidt tolerance factor,* which also expressed the degree of structural distortion. **Ref 63** also shows that the temperature/tolerance factor phase diagram at fixed doping (x=0.3) contains a metal-insulator (MI) transition, and that the highest values of CMR are found in its vicinity. This paper served as a basis for most of the subsequent developments in the field, studying, for instance, the additional effect of size disorder.

The ferromagnetic metallic phases of the manganites are rather homogeneous and isotropic, with the ferromagnetic interaction between localized spins being mediated by itinerant carriers through the so-called double exchange mechanism (C. Zener, *Phys. Rev.* 82, 403 – 1951). By contrast, the insulating phases display structural inhomogeneities and anisotropies driven by the Jahn-Teller effect, either dynamically (paramagnetic phases) or statically (antiferromagnetic and ferromagnetic phases). John Goodenough (*Phys. Rev.* 100, 564 – 1955), predicted long ago the phenomenon of charge/orbital ordering in manganites, based on their unusual magnetic ordering, but his predictions were never verified experimentally. By using a combination of synchrotron X-ray and neutron powder diffraction, PGR discovered the first, incontrovertible evidence of this extremely important effect, first in $La_{0.5}Ca_{0.5}MnO3$ – **Ref 88** and then $La_{0.333}Ca_{0.667}MnO_3$ – **Ref 106** (809 cit. and 200 cit., respectively), providing at the same time detailed structural models of the associated structural distortions, which, after many years, still stand the test of time.

In manganites with intermediate tolerance factors, a weak MI transition occurs upon ferromagnetic ordering. In **Ref 74** (253 cit.), PGR established the first experimental link between static and dynamic MnO_6 octahedral distortions (-Teller polarons) and charge mobility. At constant temperature, this transition can be driven by an external magnetic field, producing a large magnetoresistance. However, truly "colossal" CMR has a different origin. In **Ref 93** (249 cit.), by using synchrotron X-ray powder diffraction, PGR showed, for the first time, clear evidence that these CMR effects are due to *electronic phase segregation* and percolation, previously proposed theoretically both in high-T_c and in manganites, but never before experimentally observed.

Superconductors

At the beginning of his career in the early 90', PGR had focussed his research on high-T_c superconductivity, first with the Argonne group of J.D. Jorgensen and later with the Grenoble group of M. Marezio. By then, an enormous number of cuprate superconductors had been synthesised, with new discoveries being reported almost daily. There was a desperate need for systematic structural studies, carried out on exquisite samples with state-of-the-art techniques, which could extract a few key parameters for superconductivity from a plethora of different structural types. PGR's early work, with a special emphasis on the roles of phase transitions and related structural distortions and of defect chemistry, has been extremely influential across several communities, and has been used as the basis for countless calculations and theories.

$La_{2-x}Sr_xCuO_4$ (LASCO) was then and remains now the *drosophila* of high-T_c superconductors, especially regarding the link between structure and superconductivity. For instance, in a 1992 PRL, the Bell Labs group had proposed that superconductivity could only exist in the orthorhombic phase. In **Ref 54** (320 cit.), PGR conclusively proved that this is not the case, presenting a detailed study of the LASCO structure as a function of temperature and doping by neutron powder diffraction. **Ref 54** remains the definitive archival paper on this subject.

Among the new high-T_c families, Hg-based cuprates are peculiar, not only for their record T_c, but also because of their structural simplicity. PGR co-authored the first neutron investigations on these materials, identifying the doping site and mechanism (e.g., **Ref 47**, 154 cit.). After moving to Grenoble, PGR solved what was then main outstanding puzzle on Hg cuprates. All high-T_c superconductors contain MO_x metal oxide blocks, as well as one or more CuO_2 layers. Materials with *single* and *double* BiO_x or TlO_x blocks existed, but only single-Hg-layer materials had been made thus far. In **Ref 57** (41 cit.) PGR describes the design and synthesis by high-pressure techniques of the first (and only) double-Hg-layer superconductor, $Hg_2Ba_2(Y,Ca)Cu_2O_{8-\delta}$. This paper also contains a comprehensive neutron powder diffraction study, in which the complex defect structure of this material is described and related to its relative low T_c (~70 K).

Summary

The significance of PGR work on transition metal compounds can be gauged by consulting a contemporary condensed matter physics textbook, such as Daniel I. Khomskii, *Transition Metals Compounds*, Cambridge University Press (Cambridge, UK), 2014. PGR's work on charge/orbital ordering in manganites (**Refs 88, 106**) and on magnetite (**Ref 118**) are described in Chapter 7. Chapter 8 describes ferroaxial multiferroics (**Refs 169, 171**) and collinear multiferroics (**Ref 128**). MI transitions in spinels (**Refs 119, 126**) are described in Chapter 10.