Molecular-based magnets: setting the scene

By Peter Day[1] and Allan E. Underhill[2]

[1]*Davy Faraday Research Laboratory, The Royal Institution of Great Britain,*
21 Albemarle Street, London W1X 4BS, UK
[2]*School of Chemistry, University College of North Wales, Bangor,*
Gwynedd LL57 2DG, UK

In 1839, when Michael Faraday published the first picture of the lines of magnetic flux around a magnet (Faraday 1832), shown in figure 1, the cylinder of material in the centre of the figure could only have been one material, iron. Over the succeeding 160 years, the number of substances showing spontaneous magnetization has increased enormously, while their variety has broadened dramatically. Yet till quite recently, the field of magnetic materials has been traditionally confined to metals, among which the current 'market leaders' such as lanthanide–cobalt and Nd–Fe–B have achieved large technological significance. Among non-metallic phases, transition metal oxides made an early appearance in the years immediately before and after World War II, and the technologically driven need to understand and optimize their properties led to the phenomenological theories of Néel, complemented later by the microscopic models of Mott (1949), Anderson (1963) and Goodenough (1955). The latter, in particular, set out the orbital symmetry rules that brought the subject of cooperative magnetism firmly within the ambit of the solid-state chemist.

Halides, chalcogenides and pnicnides are for the most part continuous lattice compounds, and, apart from isolated instances that could be regarded more or less as curiosities (such as diethyldithiocarbamato–Fe(III) chloride (Wickman *et al.* 1967*a*, *b*) and Mn phthalocyanine (Barraclough *et al.* 1970)), magnetic solids built up from molecular coordination or organometallic complexes only arrived on the scene quite recently. Early work by the Dutch school (de Jongh & Miedema 1974) had shown that layer perovskite halide salts of Cu(II) were useful models for ferromagnetism in insulating two-dimensional lattices, while we found that by replacing Cu ($S = 1/2$) with Cr ($S = 3/2$) organic intercalated insulating ferromagnets could be synthesized with Curie temperatures up to 50 K (Bellitto & Day 1976; for reviews see Day (1986) and Bellitto & Day (1992)). These Cu(II) and Cr(II) salts were also excellent realizations of the ferromagnetic exchange arising from orthogonality between orbitals on neighbouring metal centres containing the unpaired electrons, of the kind pointed out by Goodenough (1963) and Kanamori (1959) for continuous lattice oxides. Organometallic charge transfer salts and one-dimensional ferrimagnetic coordination polymers followed in the 1980s (Miller *et al.* 1988; Nakatami *et al.* 1991), while the early 1990s saw the first ferromagnets made from purely organic molecular building blocks, without any metal atoms at all, heralding a new field of p-electron magnetism to complement that of d- and f-electron materials (Tamura *et al.* 1991).

Given the truly enormous number of magnetic solids prepared, characterized and exploited in the last century or so, it is legitimate to ask what new features, either

Phil. Trans. R. Soc. Lond. A (1999) **357**, 2851–2853

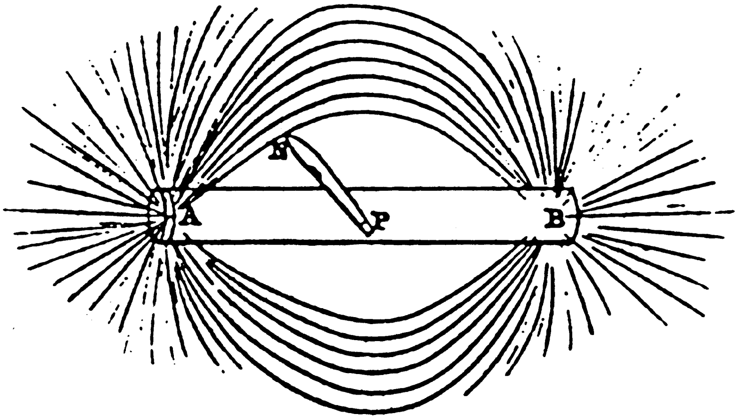

Fig. 25.

Figure 1. The first published picture of lines of magnetic flux around a magnet (Faraday 1832).

experimental or theoretical, the molecular-based materials have brought to this field. There are many. From the point of view of synthesis and processing, the contrast with conventional magnetic materials could not be more stark: substances made at (or close to) ambient temperature, usually from solution compared with high temperature metallurgical or ceramic processes. A real chance exists to make a soluble magnet! Correlating magnets with other properties, it should be pointed out that all known molecular-based magnetic compounds are insulators, the precise inverse of the situation for continuous lattice materials. That simple fact has consequences for many of the accompanying properties, of which the most striking (and potentially one of the most useful) is optical. The molecular-based materials are frequently transparent to infrared and visible light. More than 20 years have passed since we first demonstrated the striking colour change occurring in an insulating ferromagnetic transition metal salt on passing through the Curie temperature as a result of coupling excitons to spin waves (Bellitto & Day 1978; Bellitto *et al.* 1980). Combining magnetism with properties only found in the molecular solid state, such as mesomorphism or chirality, would appear to be another potentially fruitful source of novel physics, as is the construction of unusual lattice topologies, such as the Kagomé lattice, with which to test statistical thermodynamic models of critical behaviour. One apparent drawback of molecular-based magnetic materials, especially in the realm of information storage, is that the large majority are very soft magnets, i.e. they have quite low coercivities. However, even this limitation is now being breached, as two contributions to this issue demonstrate (Kahn, this issue; Kurmoo, this issue).

In all, the design, synthesis and study of molecular-based metal-organic and organic magnets has brought supramolecular and coordination chemistry, as well as purely organic synthetic chemistry to bear on a field previously dominated by condensed matter physics. In doing so, it has given new impetus to these fields and provided physics with new objects for study. While technological spin-off is in its infancy, it can confidently be predicted that new applications not replacing, but complementing, existing materials are not far away. It is to be hoped that the present collection of contributions, stemming from the lively Discussion Meeting organized under the auspices of the Royal Society and held on 24–25 March 1999, will be of wide interest to chemists and physicists, and will serve to broaden appreciation of this fascinating multidisciplinary topic.

References

Anderson, P. W. 1963 *Sol. State Phys.* **14**, 99.

Barraclough, C. C., Martin, R. L., Mitra, S. & Sherwood, R. C. 1970 *J. Chem. Phys.* **53**, 1638.

Bellitto, C. & Day, P. 1976 *J. Chem. Soc. Chem. Commun.*, p. 870.

Bellitto, C. & Day, P. 1978 *J. Chem. Soc. Chem. Commun.*, p. 511.

Bellitto, C. & Day, P. 1992 *J. Mater. Chem.* **2**, 265.

Bellitto, C., Fair, M. J., Wood, T. E. & Day, P. 1980 *J. Phys.* C **13**, L627.

Day, P. 1986 *J. Mag. Mag. Mat.* **54–57**, 1273.

de Jongh, L. J. & Miedema, A. R. 1974 *Adv. Phys.* **23**, 1.

Faraday, M. 1832 *Phil. Trans. R. Soc. Lond.* **122**, 125.

Goodenough, J. B. 1955 *Phys. Rev.* **100**, 564.

Goodenough, J. B. 1963 *Magnetism and the chemical bond.* Intrascience: New York.

Kanamori, J. 1959 *J. Phys. Chem. Solids* **10**, 87.

Miller, J. S., Epstein, A. J. & Reiff, W. M. 1988 *Chem. Rev.* **88**, 201.

Mott, N. F. 1949 *Proc. Phys. Soc.* A **62**, 416.

Nakatami, K., Bergerat, P., Codjovi, E., Mathionière, C., Pei, Y. & Kahn, O. 1991 *Inorg. Chem.* **30**, 3977.

Tamura, M., Nakazawa, Y., Shiomi, D., Nozawa, K., Hosokoshi, Y., Ishikawa, M., Takahashi, M. & Kinoshita, M. 1991 *Chem. Phys. Lett.* **186**, 401.

Wickman, H. H., Trozzolo, A. M., Williams, H. J., Hull, G. W. & Merritt, F. R. 1967*a* *Phys. Rev.* **155**, 563.

Wickman, H. H., Trozzolo, A. M., Williams, H. J., Hull, G. W. & Merritt, F. R. 1967*b* *Phys. Rev.* **163**, 526.