Magnetoelectricity and multiferroics

Charles Simon
Laboratoire CRISMAT, CNRS and ENSICAEN, F14050 Caen.

Introduction :

The possibility for a material to be both ferromagnetic and ferroelectric was predicted by P. Curie in 1894. The coupling term which modifies the magnetization by application of electric field (or the reverse) was predicted at the same time by an analysis of the Landau expansion of the free energy (Landau and Dzyaloshinskii 1960) and rapidly observed experimentally (Folen 1961). However, this field was also rapidly decreasing, because the number of compounds which belong to this class is small. Two reasons explain this small number of compounds: the origin of dipolar moments is often related to d^0 electrons, the magnetic moments of these electrons being zero. In addition, the number of magnetic and crystallographic space groups is very small (Hill 2000).
However, the presence of incommensurate modulations suppresses number of symmetry elements and allows being multiferroic. In addition, for practical applications, the existence of exchange bias phenomenon allows to use antiferromagnetic materials for the storage of information. We should extend our study to antiferromagnetic materials.

Definition

In this lecture, a "multiferroic" material presents both ferroelectric and ferromagnetic properties. Magnetoelectricity is the possibility to induce current by variation of the magnetic field.

Symmetry

The analysis of the symmetry of the system allows writing the Landau expansion of the free energy of the system including the two order parameters polarization P and magnetization M as function of electric field E and magnetic field B.

In order to have both possibility of spontaneous M and P, there are 31 point groups that allow a spontaneous polarization and 31 that allow a magnetization. 13 point groups (1,2,2',m,m',3,3m',4,4m'm',m'm2',m'm'2',6 and 6m'm') are found to allow both.

This is quite restrictive, but in fact, the symmetry can be reduced and allow P and M if there is an incommensurate modulation. In this case, many possibilities exist.

Even if P and M does not exist, it exist also some materials in which P can be induced by the application of an external magnetic field and vice versa. Cr_2O_3 was the first example in the literature. Even for highly symmetric materials, a quadratic dependence on magnetic field of the dielectric constant always exists.

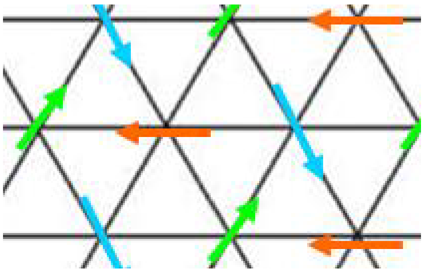
On site coupling

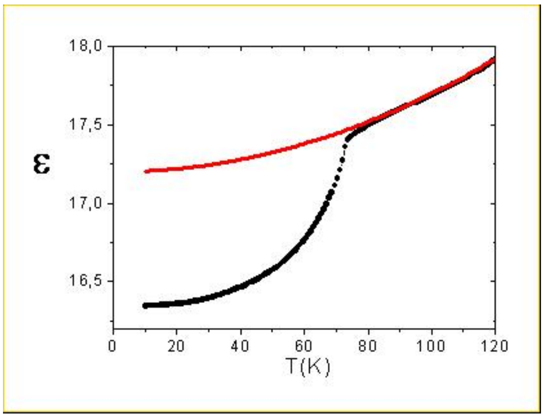
The mechanism to introduce a coupling term is always the following: application of electric field induces an atomic displacement which modifies the magnetic couplings in the magnetic structure. But most of these couplings are quadratic. The Dzyaloshinskii-Moriya interaction predicts a linear coupling which is very interesting. In literature, many different mechanisms are proposed, such as “spin currents”, but their role is not fully clear at the present time.

Some examples

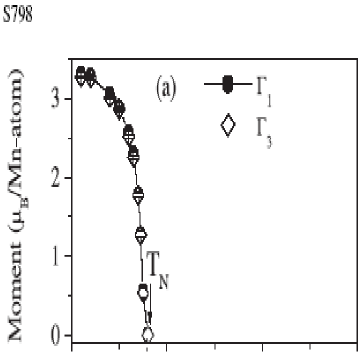
$YMnO_3$

The first example that I describe is $YMnO_3$. This compound is antiferromagnetic with a triangular structure, there is also a small perpendicular ferromagnetic component. ($P6_3cm$). The magnetic transition is about 70K. The compound is ferroelectric at room temperature and below. The polarization presents an anomaly at the magnetic transition. It is a proper ferroelectric.





Dielectric constant ε as function of temperature.

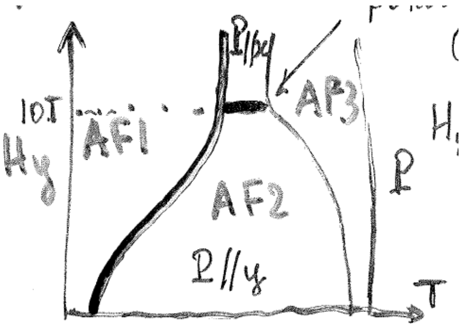


The alternate magnetization L as function of temperature (from neutron scattering.

In this system, there is a coupling between magnetization and ferroelectricity.

$MnWO_4$

This compound is an improper ferroelectric with a succession of phase transitions 13.7K, 12.7K, 7.6K in absence of magnetic field. The non magnetic space group is P2/c1’. At low temperature, AF1 phase is k=(1/4,1/2,1/2), AF2, k=(0.214,1/2,0.457) spiral with P non zero, AF3 is collinear.

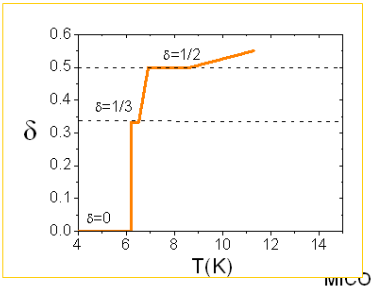


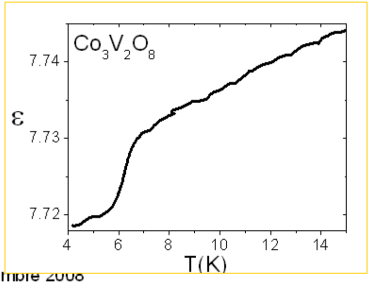
In this example, we will show how the Landau expansion can explain the different phases without and with applied magnetic field (after P. Toledano).

$Co_3V_2O_8$

(N. Bellido)

In this compound, there is a succession of incommensurate phases, which are ferroelectric. The commensurate low temperature phase is not.



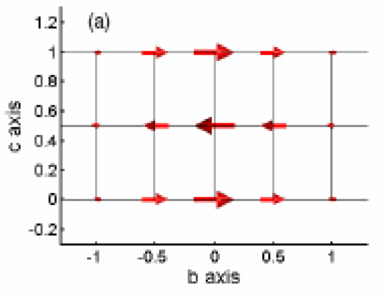


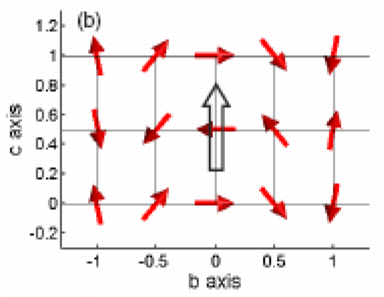
Incommensurability parameter of the magnetic structure versus temperature

Dielectric constant versus temperature

$TbMnO_3$

$TbMnO_3$ is a pseudo-proper ferroelectric, with electric polarisation along y in phase II. The space group is Pnma with a propagation vector k=(δ,0,0).

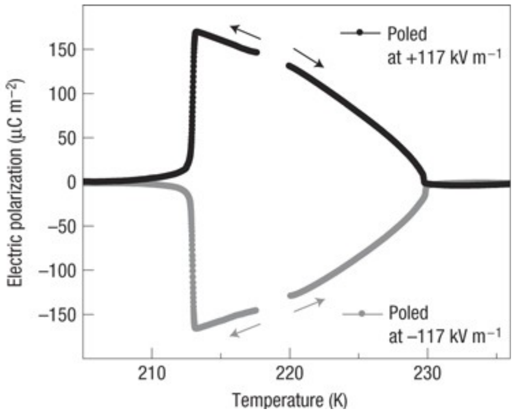




CuO

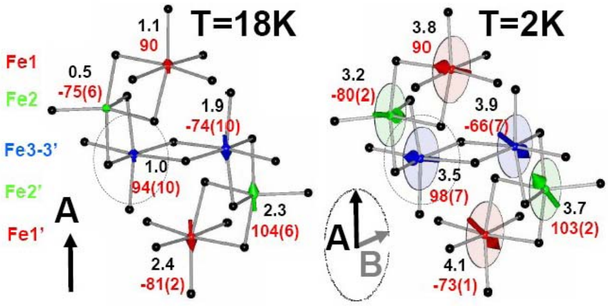
(Kimura 2008)

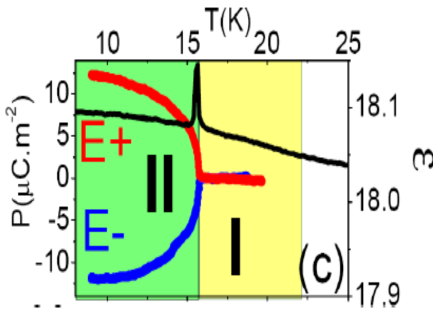
This system presents quite high temperature improper ferroelectricity.



$FeVO_4$

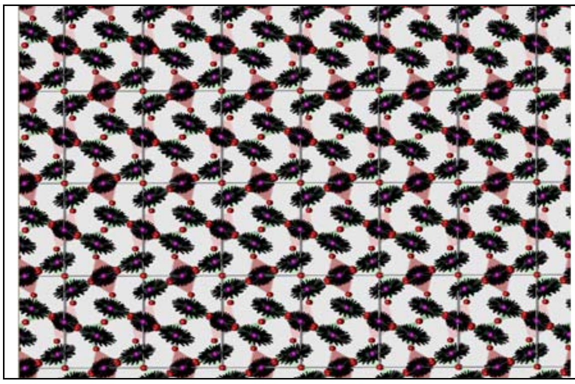
(Daoud-Aladine 2009)
This system is 1’, the lowest symmetry, everything is possible… Ferroelectricty appears below 16K.





Conclusion

The multiferroic properties are quite common in incommensurate magnetic frustrated system. The variety of behaviours is immense. This field is a marvellous and complex playground for physicists.

	A nice example with Mn^{3+} and Mn^{4+}. From P. G. Radaelli,C. Vecchini,L. C. Chapon,P. J. Brown,S. Park,and S-W. Cheong, Phys. Rev. B 79, 020404R (2009). (YMn_2O_5).

Acknowledgements

The examples are taken in the work of my colleagues M. Poienar, D. Saurel, N. Bellido, K. Singh and B. Kundys who was my collaborator during these last years. Many discussions with A. Maignan, C. Martin and M. Lepetit were very useful.

References

V. J. Folen, G. T. Rado, and E. W. Stalder, Phys. Rev. Lett. **6**, 607 (1961).
N. A. Hill, J. Phys. Chem. B **104**, 6694 (2000).
I. E. Dzyahoshinskii, Sov. Phys. JETP 10, 628 (1960).
D. N. Astrov, Sov. Phys. JETP 11, 708 (1960).
M. Mostovoy, Phys. Rev. Lett. 96, 067601 (2006).
T. Kimura et al., Nature Materials 7, 291 - 294 (2008)
A. Daoud-Aladine, B. Kundys, C. Martin, P.G. Radaelli, P.J. Brown, C. Simon, L. C. Chapon, arXiv:0812.4429v1, Phys.Rev.Lett. (submitted) (2009).
G. Lawes, A. B. Harris, T. Kimura, N. Rogado, R. J. Cava, A. Aharony, O. Entin-Wohlman, T. Yildrim, M. Kenzelmann, C. Broholm, and A. P. Ramirez, Phys. Rev. Lett. 95, 087205 (2005).
T. Kimura, J. C. Lashley, and A. P. Ramirez, Phys. Rev. B 73, 220401(R) (2006).
M. Kenzelmann et al., Phys. Rev. Lett. 95, 087206 (2005)
E. du Trémolet de Lacheisserie, Magnetostriction: Theory and Application of Magnetoelastisity (CRC Press, Boca Raton, FL,) (1993).
T. Kimura, G. Lawes, T. Goto, Y. Tokura, and A. P. Ramirez, Phys. Rev. B 71, 224425 (2005).
T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Nature (London) 426, 55 (2003).
B. Kundys, A. Maignan, Ch. Simon, Appl. Phys. Lett. 94, 072506 (2009).
N. Bellido, C. Simon, and A. Maignan, Phys. Rev. B **77**, 054430 (2008)