

the observation that most multiferroics are ferroelectric antiferromagnets, Binek and Doudin⁹ suggested focusing on exchange bias, the directional coupling occurring at the interface between a ferromagnet and an antiferromagnet. This proposal triggered much activity in the search for exchange bias using multiferroics, its connection to ferroelectric properties¹⁰ and ultimately its electrical control. Interesting results on the manipulation of exchange bias have been reported by Laukhin *et al.*, but with the low-temperature multiferroic YMnO_3 (ref. 11).

However, the number of multiferroics that could be used for MERAMS is quite limited, and so far only BiFeO_3 (BFO) has emerged as a potential candidate. In bulk, BFO is a rhombohedral perovskite, exhibiting antiferromagnetism with a Néel temperature of 640 K and ferroelectricity up to 1,100 K (ref. 12). A magnetoelectric coupling between the two order parameters has been demonstrated recently¹³. Its large electrical polarization¹², the highest among all known ferroelectrics, already makes BFO a strong candidate

for next-generation FeRAMs¹⁴. As now shown by Chu *et al.*, BFO also seems very promising for the design of future MERAM elements. Indeed, they report for the first time a magnetoelectric manipulation of magnetization at room temperature.

In BFO, the ferroelectric polarization and the antiferromagnetic vector are coupled¹³, so that reversing the polarization by an electric field also rotates the antiferromagnetic spins. In line with the above MERAM scheme, Chu *et al.* show that the ferromagnetic domain structure of CoFe micrometre-size elements deposited on top of a BFO film also exhibits a systematic coupling with the antiferromagnetic spins in BFO. Therefore, when an in-plane electric field is applied, the magnetic domain structure of the CoFe dots is modified as the magnetization rotates by 90 degrees. The original magnetic state is recovered when a voltage with opposite polarity is applied.

This result is an essential step towards the fabrication of prototype MERAM elements that are reproducibly switched by an electric field. However, many issues

remain, as for future devices a perpendicular geometry, low write voltages, high-frequency operation (GHz) and nanoscale devices will eventually be needed. Now, the next step is to realize a full MERAM element where the electrical resistance of a spintronics device is controlled with a multiferroic. Nevertheless, the control of magnetism by a multiferroic achieved by Chu and colleagues is certainly a testament to the rude health of this field, and extends the potential of multifunctional oxides for novel devices.

References

1. Eerenstein, W., Mathur, N. D. & Scott, J. F. *Nature* **442**, 759–765 (2006).
2. Kimura, T. *et al.* *Nature* **426**, 55–58 (2003).
3. Hur, N. *et al.* *Nature* **429**, 392–395 (2004).
4. Chu, Y.-H. *et al.* *Nature Mater.* **7**, 478–482 (2008).
5. Gajek, M. *et al.* *Nature Mater.* **6**, 296–302 (2007).
6. Yang, F. *et al.* *J. Appl. Phys.* **102**, 044504 (2007).
7. Albert, F. J. *et al.* *Appl. Phys. Lett.* **77**, 3809–3811 (2000).
8. Kawahara, T. *et al.* *IEEE J. Solid State Circuits* **43**, 109–120 (2008).
9. Binek, C. & Doudin, B. *J. Phys. Condens. Matter* **17**, L39–L44 (2005).
10. Béa, H. *et al.* *Phys. Rev. Lett.* **100**, 017204 (2008).
11. Laukhin, V. *et al.* *Phys. Rev. Lett.* **97**, 227201 (2006).
12. Lebeugle, D. *et al.* *Phys. Rev. B* **76**, 024116 (2007).
13. Zhao, T. *et al.* *Nature Mater.* **5**, 823–829 (2006).
14. Maruyama, K. *et al.* *Fujitsu Sci. Tech. J.* **43**, 502–507 (2007).

COMPUTATIONAL MATERIALS SCIENCE

Out of the scalar sand box

With the extension of a popular computational method to its tensorial analogue, structural configurations that optimize anisotropic physical quantities can now be predicted.

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A primary goal of materials science is to discover or design new materials that meet societal needs. In computational materials science, we aim to achieve this goal by directly modelling materials from first principles if possible. We can do this in essentially all cases where the structure of the target material is known. Knowing only the location of the atoms in space and in the periodic table, a wide variety of important quantities, such as piezoelectricity, non-collinear magnetism, and electron–phonon coupling, can be calculated using off-the-shelf codes. However, in many (perhaps most?) of the relevant problems, the real issue is more the opposite, that is, finding the stable structure or a structure for which certain properties are optimized.

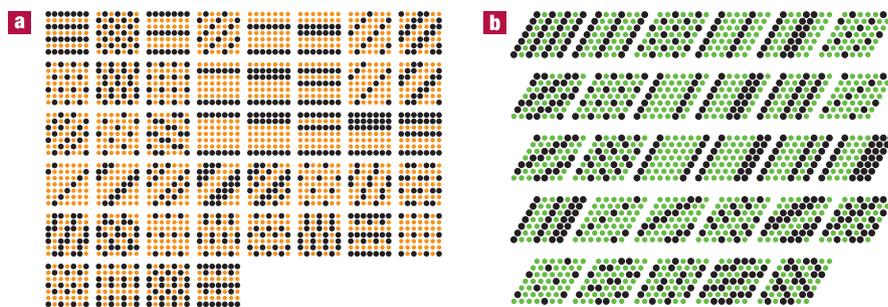


Figure 1 Binary atomic configurations. **a**, All possible binary configurations for two types of atoms on a square lattice with up to six atoms per cell. Only symmetrically distinct cases are illustrated. **b**, The same diagram for hexagonal lattices. The cluster expansion can quickly predict configuration–property relationships for millions of such derivative structures¹² to find optimal configurations.

General structure prediction, either from first principles or other means^{1–5}, is extremely challenging simply because the parameter space of structures is so vast. As a consequence, predicting materials

properties as a function of structure is also quite difficult. One powerful approach to calculating structure–property relationships is the cluster expansion^{6–10}. The cluster expansion is usually used to model the

configurational dependence of scalar quantities, such as formation enthalpies, bandgaps, bulk moduli, Curie temperatures and so on. On page 455 of this issue, Axel van de Walle presents a profound extension of this method¹¹. The extension allows prediction of anisotropic properties, that is, tensor properties such as elasticity, optoelectronic coupling and piezoelectricity.

The cluster expansion approach is particularly effective when the structural question is one of 'configuration' rather than location (see Fig. 1). For example, in nickel-based superalloys the atomic sites essentially constitute a body-centered-cubic lattice. The arrangement, or ordering, of nickel, aluminium, or impurity atoms, or even vacancies, on those b.c.c. sites profoundly influences the performance of the alloy, and the best energetic preferences can be accurately predicted via cluster expansion.

The cluster expansion method can be used to calculate, essentially instantly and with first-principles accuracy, the target property for any atomic configuration. Because computing the target quantity is so efficient, the cluster expansion can be used in thermodynamic simulations or kinetic Monte Carlo modelling. With van de Walle's extension to the method it can now be applied to a much broader range of target properties. The significance goes beyond a mere algorithmic advance — it's likely to make a real difference in computational-based materials design. The cluster expansion has so far been used to predict maximum bandgaps, maximum critical temperatures in magnetic semiconductors, and so on. But finding an atomic configuration that

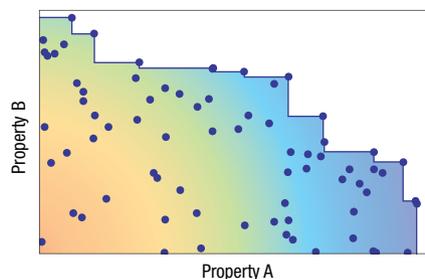


Figure 2 Illustration of how the tensorial cluster expansion can be used in practical materials design problems. After calculating the values of property A and B for all possible atomic configurations, one constructs the 'Pareto front'. Knowing the Pareto front, a materials engineer can select nature's best solution to maximizing competing requirements for a particular application.

optimizes a target quantity is a far cry from actually making such a material. One cannot simply 'build' a compound with an arbitrary arrangement of atoms on a given lattice — nature dictates that free-energy minimization ultimately determines the atomic configuration. But van de Walle's approach will be useful in epitaxial systems in which materials scientists can make metastable structures, where some control over the atomic configuration is possible.

Van de Walle's tensorial cluster expansion will be useful in epitaxial systems because many of the target properties of interest are anisotropic and cannot be treated with a standard scalar cluster expansion. The most exciting aspect of this new method is that

one can immediately see how it could be used in a practical materials design problem. Imagine a material with two properties A and B that one wishes to maximize but which are competing — maximizing one decreases the other and *vice versa*. Such 'trade off' problems are inevitable in materials applications. Using the tensorial cluster expansion one could determine the best possible compromise (Fig. 2). After calculating property A and B for every experimentally realizable configuration, one simply constructs the Pareto front to find the best possible trade-offs between A and B irrespective of any application-limited requirements on either property.

The authors' findings are exciting because of the potential to bring together first-principles modelling with practical materials design. The extension of a well-established computational method to a new class of properties is sure to open unanticipated avenues of exploration.

References

1. Fischer, C. C., Tibbetts, K. J., Morgan, D. & Ceder, G. *Nature Mater.* **5**, 641–646 (2006).
2. Curtarolo, S., Morgan, D. & Ceder, G. *Calphad* **29**, 163 (2005).
3. Abraham, N. L. & Probert, M. I. J. *Phys. Rev. B* **73**, 224104 (2006).
4. Oganov, A. R. & Glass, C. W. J. *Phys. Condens. Matter* **20**, 064210 (2008).
5. Wolverton, C. & Zunger, A. *Phys. Rev. Lett.* **81**, 606–609 (1998).
6. Sanchez, J. M., Ducastelle, F. & Gratias, D. *Physica A* **128**, 334–350 (1984).
7. de Fontaine, D. *Solid State Phys.* **47**, 33–176 (1994).
8. Muller, S. J. *Phys. Condens. Matter* **15**, R1429–R1500 (2003).
9. Hart, G. L. W., Blum, V., Walorski, M. & Zunger, A. *Nature Mater.* **4**, 391–394 (2005).
10. Zunger, A. in *Statics and Dynamics of Alloy Phase Transitions* (eds Turchi, P. E. A. & Gonis, A.) 361–419 (NATO ASI Series, Ser. B, Plenum Press, New York, 1994).
11. van de Walle, A. *Nature Mater.* **7**, 455–458 (2008).
12. Hart, G. L. W. & Forcade, R. W. *Phys. Rev. B* (in the press); preprint at <<http://arXiv.org/abs/0804.3544v1>> (2008).

CONJUGATED POLYMERS

What makes a chromophore?

The spectral complexity shown by conjugated polymers has been explained by interactions between chromophores in tangled chains, but experiments on model oligomers reveal that it may arise from the chromophores themselves.

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Conjugated polymers, such as poly(phenylene vinylene) derivatives (Fig. 1a), are remarkable materials: they combine the electrical properties of semiconductors with the mechanical

properties of plastics. These materials can be processed inexpensively by techniques such as spin-coating and ink-jet printing, and they are already finding application in optoelectronic devices such as plastic light-emitting diodes (LEDs¹) and photovoltaic cells². Yet, despite their enormous practical potential and years of study, it has not been clear how best to think about the electronic properties of conjugated polymers. The typical picture

of their electronic structure has been that electronic excitations on each chain are confined to separate, rigid chromophores that act largely independently, and that most of the electronic complexity is a consequence of interactions between chromophores, or interchain effects. This picture, however, has been challenged recently by Becker *et al.*, who report in the *Journal of Physical Chemistry B* that much of the spectral complexity associated