



50 Years Ago

A chain of ecological events extraordinary for the British Isles is reported in this week's issue of *Nature* ... They concern the unusual bloom of a planktonic alga, the dinoflagellate *Gonyaulax tamarensis*, off the Northumbrian coast of Britain in May this year. This eventually led to the illness of more than eighty people through mussel poisoning and the deaths of about 80 per cent of the breeding population of shags on the Farne Islands ... Fortunately for the mussel eaters of Northumberland, most of the mussels eaten had been well cooked, the juices had been drained away, and in this way some of the poison was eliminated. Otherwise there would probably have been much more serious effects and even some deaths.
From *Nature* 5 October 1968

100 Years Ago

In North Wales, on August 20 ... I saw a rainbow-effect which was quite new to me. The summit of Tryfaen ... has three sharp, rocky peaks ... We had climbed up the eastern cliff in a south-westerly gale, which brought up much cloud with some light showers, and were sitting just below the top of the southern peak. The Holyhead road lay north-east and 2000 ft. below us. From it rose the upright portion of a brilliant rainbow. At the centre of its circle was the shadow of our peak with those of the other two peaks to the left of it, all sharply defined. Around the shadow of our peak was a most vivid and persistent bow, the smallest I have ever seen, the radius of the inner edge being about half that of the outer ... Outside this bow (which had the colours in regular rainbow order, red outside) was part of a third bow of perhaps double the diameter, but dim and intermittent.

From *Nature* 3 October 1918

patients, ideally starting at disease onset.

It would indeed be valuable to obtain a precise picture of the contribution of hypocretin-specific CD4⁺ T cells to narcolepsy. Do these cells initiate the disease-causing process? Do they contribute to the later-stage progression? Are they present as a secondary consequence of the disease but do not contribute to disease progression? There are many possibilities to consider. For example, do unidentified immune cells cause the demise of hypocretin-producing neurons and lead to a second wave of immune cells, such as hypocretin-specific T cells, that target the neurons? Or perhaps such second-wave T cells might not contribute to the progression of narcolepsy at all, because they might not interact with hypocretin-producing neurons.

If further experiments strengthen the proposed link between increased T-cell reactivity to hypocretin and neuronal damage, Latorre and colleagues' study might lead to targeted immune therapies. If this is the case, such treatments would probably be developed to target the immune system at the time of onset of narcolepsy. ■

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MATERIALS SCIENCE

Morphing into action

An organic polymer exhibits a phase transition that is associated with improved electromechanical properties. This feature links organic polymers with widely used perovskite materials, and could have many applications. SEE LETTER P.96

RONALD E. COHEN

The properties of a material can change dramatically in the vicinity of a phase transition. For example, the electromechanical properties of ferroelectric materials are greatly enhanced in a transition region known as a morphotropic phase boundary. Here, the material's electric polarization (dipole moment per unit volume) rotates from one direction to another. This phenomenon is well studied in perovskite materials, but on page 96, Liu *et al.*¹ report similar behaviour in an organic polymer. The discovery could open up various applications, such as in medical instruments, power-generating clothes and improved safety devices for structures and vehicles.

Active materials transform energy from one type into another. For example, ferroelectrics convert electrical energy into mechanical energy, and vice versa. Ferroelectrics are used

in technologies ranging from medical ultrasound systems to fuel-injection and crash-sensing equipment in cars. They even have applications in refrigeration and the generation of power from excess heat.

The most commonly used ferroelectric is the perovskite lead zirconate titanate (PZT). Although PZT is cheap, it contains toxic lead and is a hard ceramic that can be produced only at high temperatures. The lead content limits the material's use in applications such as tiny pumps, and motors that are permanently installed in the human body. Single-crystal 'relaxor' ferroelectrics have also been developed. These materials have much higher energy-conversion efficiencies than PZT and are advancing the resolution of medical ultrasound systems, for example. But they are much more expensive than PZT, and also contain lead.

In addition, there are active materials based on lead-free polymers. These materials can

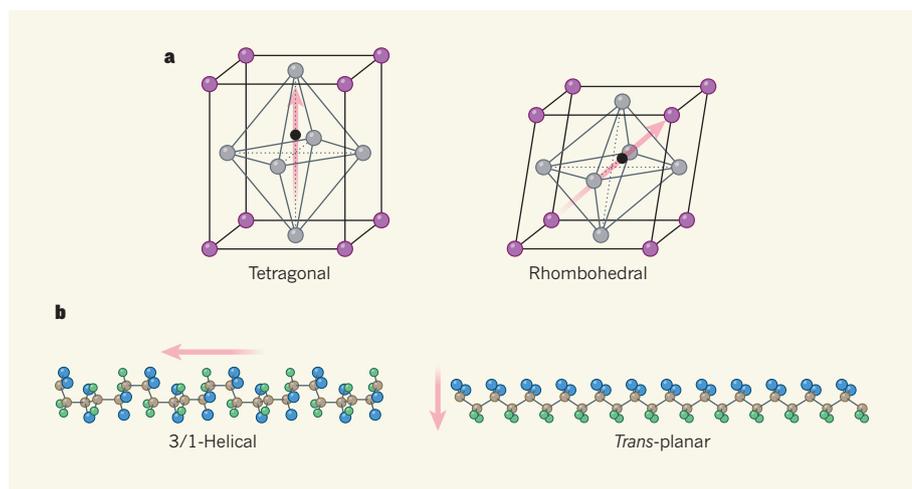


Figure 1 | Two types of phase transition. **a**, The inorganic material lead zirconate titanate (PZT) has different electric polarizations (arrows) on the two sides of a phase transition. Away from the transition region, PZT is tetragonal on the titanium-rich side and rhombohedral on the zirconium-rich side. In the transition region, the polarization rotates between the two different directions, and the material exists in intermediate (monoclinic) phases (not shown). The transition is termed morphotropic because of these shape changes. Purple, lead; grey, oxygen; black, titanium or zirconium. **b**, Liu *et al.*¹ report a similar type of phase transition for the organic polymer poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)). VDF-poor compositions of this material exist in what is known as a 3/1-helical phase, with a polarization that points along the axis of the polymer chains. VDF-rich compositions are in a *trans*-planar phase, with a polarization that is perpendicular to the chains. For simplicity, structures are shown for chains of VDF, rather than for P(VDF-TrFE). Brown, carbon; blue, fluorine; green, hydrogen.

be produced inexpensively and moulded in a similar way to plastics, but have much lower energy-conversion efficiencies than PZT. Now, Liu and colleagues have demonstrated a way to boost the efficiencies of polymer ferroelectrics, making these materials more competitive with conventional, inorganic ferroelectrics.

The temperature–composition phase diagram of PZT was established in the 1950s². It has an almost-vertical morphotropic phase boundary (MPB), positioned where the ratio of titanium to zirconium is about 50:50. On the titanium-rich side of the boundary, PZT has a tetragonal perovskite structure, whereas on the zirconium-rich side, it has a rhombohedral perovskite structure (Fig. 1a).

The idea of an MPB goes back to the nineteenth century, and is not restricted to perovskites. A paper from 1890 discusses the origin of the term morphotropic³, and suggests that it was coined in 1870 by the mineralogist Paul Heinrich von Groth⁴ — who, incidentally, founded the scientific journal *Zeitschrift für Kristallographie und Mineralogie* and was a professor of mineralogy and curator of minerals in Munich.

The word morphotropic is related to polymorphic. Polymorphs are different crystal structures of compounds that have the same chemical composition — such as graphite and diamond, which are both forms of carbon. A phase boundary between such different polymorphs is not useful for applications of active materials. This is because the phases can exist in a metastable form far from the region of the phase diagram in which they are stable.

Consequently, for example, diamonds can exist on Earth's surface and can even be grown in a metastable form at low pressures.

By contrast, an MPB describes a transition that occurs smoothly, with the crystals changing shape through the transition⁵. Today, MPBs are most commonly thought of in the context of inorganic perovskites. But Groth originally applied the term to organic crystals, such as benzene, as different chemical replacements are being made — for example, switching chlorine atoms with hydrogen atoms⁴. In the past few decades, the importance of morphotropic to organic crystals has been rediscovered and re-emphasized⁶.

Liu and colleagues considered the ferroelectric polymer system poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)), and synthesized systems that had a range of vinylidene fluoride (VDF) contents. They found that VDF-poor compositions existed in what is known as a 3/1-helical phase, whereas VDF-rich compositions were in a *trans*-planar phase (Fig. 1b). The electromechanical properties of the material were maximal in the transition region between these two phases, similar to what happens at the MPB in inorganic perovskites.

Close analogies for P(VDF-TrFE) among perovskites are relaxor ferroelectrics, such as lead magnesium niobate–lead titanate (PMN-PT). In PMN-rich compositions of PMN-PT, and in pure PMN, a ferroelectric phase is not observed because the atoms are displaced from lattice sites in a disordered manner. Similarly, Liu *et al.* saw no ferroelectric phase in VDF-poor compositions of

P(VDF-TrFE) as a result of disorder in the polymer chains.

In the case of perovskites, it was discovered in the past few decades that the simple picture of a boundary between different structural phases needs to be replaced with a transition region in which the materials exist in intermediate (monoclinic) phases^{7,8}. In this region of the phase diagram, the direction of the material's polarization rotates with varying composition, applied electric fields or stresses.

It was also found that varying composition is not required to generate behaviour akin to an MPB, and that even pure lead titanate exhibits such behaviour⁹. More specifically, lead titanate changes shape from tetragonal to rhombohedral through monoclinic intermediates under pressure. In the transition region, theory predicts that the coupling between electrical and mechanical energy will be extremely high — larger than that of known materials at ambient pressure¹⁰.

At first glance, P(VDF-TrFE) might seem about as different from perovskites as possible, but the concept of polarization rotation also holds in this polymer system. In one phase, the polarization points along the axis of the polymer chains, whereas in the other phase, it is perpendicular to the chains. The polarization direction rotates in the MPB region^{11–14}.

Now that behaviour reminiscent of an MPB has been observed in an organic molecular system, the question arises of whether similar behaviour might be induced by applying stress or electric fields, rather than by changing the chemical composition. Moreover, realizing such an effect using strain could enable materials to be easily tuned, giving rise to even more potential applications. ■

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