Condensed-matter physics

Taking the frustration out of ice

Mark Harris

Ferromagnetism — the ability of solids such as iron to be magnetized permanently — is the most familiar manifestation of magnetic order. It arises from a spontaneous alignment of the atomic magnetic dipoles (spins), driven by magnetic interactions between the atoms. But some magnetic solids display far more spectacular consequences of these interactions, particularly those that are geometrically frustrated. Put simply, this is the inability of magnets with certain crystal structures to attain magnetic order, solely by virtue of the geometrical arrangement of the magnetic atoms. The resulting behaviour is complex and rich in subtleties, pushing at the boundaries of our understanding of what constitutes crystalline order. It has implications far beyond magnetism — uniting many diverse problems, from the origin of freezing and glassiness to neural networks. Indeed, high-temperature superconductivity is believed by some to be due to a kind of frustrated magnetic state[1]. But progress in the field has been slow, hampered by the experimental difficulties of isolating the frustration from other perturbations, such as defects, which are present in all real materials. On page 333 of this issue, Ramirez and co-workers[2] present convincing evidence that the pyrochlore compound $Dy_2Ti_2O_7$ corresponds to a new class of frustrated magnet called 'spin ice', which appears to be the cleanest laboratory yet for studying frustration.

Many magnetic materials in nature are antiferromagnetic, in which the spins find an ordering pattern where each is aligned antiparallel to its neighbours. Before the discovery of spin ice, only antiferromagnetic materials were considered eligible for frustration. To illustrate, consider how spins behave when placed at the corners of some common structural building blocks: a square, a triangle and a tetrahedron (Fig. 1). With antiferromagnetic interactions it is possible for spins to align antiparallel on a square (Fig. 1a), but impossible on a triangle (Fig. 1b), because there is always one spin that cannot align antiparallel to both of its neighbours simultaneously. This inability to satisfy fully the interactions between spins — simply because of the geometry of the underlying structure — is the essence of geometrical frustration. But its effects become most severe in the pyrochlore lattice, which is composed of corner-linked tetrahedra. This can be seen from Fig. 1c, where we now find that two out of every four spins cannot align antiparallel. On the other hand, if we take ferromagnetic interactions between the spins in Fig. 1a–c, full order can be attained, because all spins can align parallel to each other. For this reason, ferromagnetism was always thought to be unfrustrated.

It was discovered that anisotropy (a further constraint on each spin's alignment, and present to varying degrees in all magnetic materials) changes the accepted picture of frustration[3], and in some cases turns it completely on its head. That is, even with the pyrochlore lattice, antiferromagnetic interactions can become unfrustrated and produce a conventionally ordered magnet, whereas ferromagnetic interactions can become strongly frustrated. This anisotropy is particularly strong in pyrochlores where the magnetic atom is a rare earth, notably Ho (holmium) and Dy (dysprosium). Here the anisotropy constrains each spin to point either directly into or away from the centre of each tetrahedron. With ferromagnetic interactions, the four spins on each tetrahedron align so that there are two pointing in and two out. One of the six possible ways of achieving this on a tetrahedron is shown in Fig. 1d. When tetrahedra are linked to form a pyrochlore lattice, the large number of ways of satisfying the 'two spins in, two spins out' rule means that no single, ordered pattern is more favourable than any other. This is another definition of frustration. In fact, it can be shown[4] that such a lattice is every bit as frustrated as any possible antiferromagnet, which came as a big surprise to those who had always blithely assumed that ferromagnetism had no surprises left.

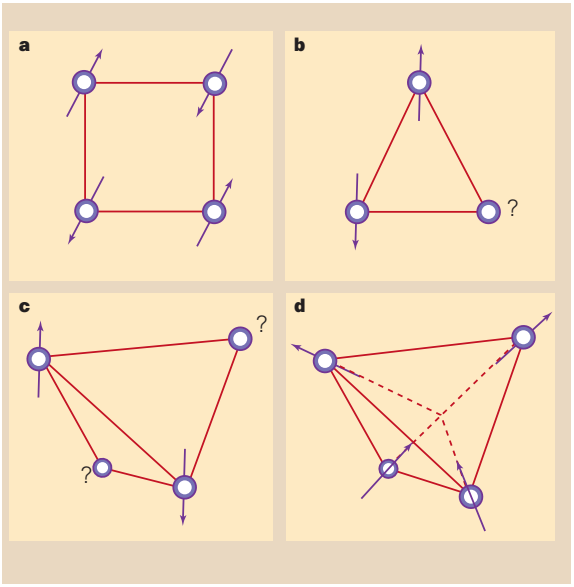

Figure 1 **Three common crystal-structure building blocks (square, triangle and tetrahedron). The circles represent magnetic atoms and the arrows magnetic spins. In** a–c **the spins are coupled by antiferromagnetic interactions, favouring antiparallel alignment of neighbouring spins. This is easy in** a, **but impossible in** b **and** c. **In** d **the coupling is ferromagnetic, but there is the additional presence of anisotropy constraining the spins to point either directly into — or away from — the centre of the tetrahedron. The resulting configuration with 'two spins in, two spins out', is a characteristic of the 'spin ice' studied by Ramirez *et al.*[2].**

More significantly, it became clear that this frustrated pyrochlore is a magnetic analogue of the old problem of how hydrogen atoms order in the ice (H_2O) lattice[3,5] (hence the nickname 'spin ice'). In this analogy, the spins represent hydrogen positions around a central oxygen atom, so 'two in, two out' corresponds to 'two hydrogens close to, and two further away' from each oxygen — the 'ice rule' that ensures the structure consists entirely of H_2O molecules. This rule does not favour one simple ordered structure, and, as Pauling realized in 1935, the number of possible structures is almost immeasurably large[6]. The entropy of ice (which is a measure of the molecular disorder of the system) was therefore expected to be finite at all temperatures down to 0 K, in agreement with the experiments of Giauque and co-workers[7]. The problem was that this finite entropy defies the third law of thermodynamics, which requires all substances to have precisely zero entropy at $T = 0$ K. Explicitly, zero entropy means there is only one equilibrium arrangement of the system of molecules.

For the past 60 years, this discrepancy has been reconciled by the proposal that the disordered arrangement does not reflect the true equilibrium state of ice at 0 K. The argument goes that if true thermodynamic behaviour could be attained, then more subtle effects would favour a unique ordered structure with truly zero entropy, and vindicate the third law. In light of the excellent agreement between Pauling's finite entropy and the value found experimentally, this might seem churlish. But there is good experimental evidence that ice is indeed out of equilibrium at low temperatures. In particular, the hydrogen-ordering dynamics are prohibitively slow below about 120 K, suggesting that some sort of glassy non-equilibrium state is formed.

Spin ice may shed new light on this issue. The best experimental realizations of spin ice are the magnetic pyrochlore compounds $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$. In 1969 it was noticed that $Dy_2Ti_2O_7$ has residual entropy at low temperatures[8]. Ramirez *et al.*[2] have uncovered a simple and beautiful result: this residual entropy is numerically in excellent agreement with the Pauling entropy for ice. So they provide the crucial link in the chain

between spin ice and water ice. This work reveals that two analogous systems — $Dy_2Ti_2O_7$ and ice — have the same entropy, even though the ordering dynamics of the spins and hydrogen atoms are vastly different. Yet these two materials still have the same statistical behaviour, pointing to a deeper truth behind Pauling's finite entropy. It is easy to believe that ice itself might be out of equilibrium, but it is harder to believe the same of $Dy_2Ti_2O_7$, because there is, as yet, no evidence of a transition into a glassy state like that of ice. One might conclude that spin ice presents a real threat to the third law of thermodynamics. That would be premature, but it certainly represents plausible evidence that the disordered state of water ice is the real ground state at low temperatures.

It would be no exaggeration to say that such a transparent and easily interpretable result has never before been obtained from a frustrated magnet. This highlights what is so appealing to the experimentalist about spin-ice compounds: despite the inevitable presence of defects and other minor perturbations that frequently dominate other frustrated magnets, an inherent purity of behaviour comes through. The link between theory and experiment is therefore much more straightforward. It is clear that, because of this, spin ice has the potential to illuminate other vexing questions arising in the past 30 years. The most urgent is the origin of glassy behaviour in chemically ordered magnets, a question that reaches into the heart of what causes glassiness in the first place. □

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Microbiology

Virus on virus infects bacterium

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Many bacteria carry segments of DNA called pathogenicity islands, which are enriched for genes encoding the proteins that contribute to virulence. Such proteins include secreted toxins, factors and signalling devices that help the bacterium to colonize its host, and even specialized types of molecular apparatus that inject bacterial products into host cells. We are starting to understand how the bacteria acquired these pathogenicity islands during evolution, and the latest findings are reported by Karaolis *et al.*[1] on page 375 of this issue. They describe a fascinating interplay between two pathogenicity islands — the first allowed the bacterium *Vibrio cholerae* to be infected with the second, which is a bacterial virus (bacteriophage) that carries the cholera-toxin genes.

Over 100 years ago, *V. cholerae* was identified as the bacterial species that causes the deadly, infectious diarrhoeal disease cholera[2]. More recently, the potent cholera toxin was found to be encoded by a filamentous bacteriophage called cholera-toxin phage (CTXΦ), which exists within *V. cholerae*[3]. The CTXΦ contains single-stranded DNA, and it uses the bacterium's main colonization pilus — an appendage used to infect the host's intestine — as its receptor[4,5]. This pilus, termed toxin co-regulated pilus (TCP), is a fibre of polymerized pilin protein termed TcpA. It promotes colonization by enhancing interactions between bacterial cells and, perhaps, directly with the host.

The TCP belongs to the type-4 family of pili, members of which are involved in colonizing diverse bacterial species[6]. As the name implies, expression of the genes that encode the TCP parallels expression of the toxin genes[7] — that is, they are expressed only when the bacterium finds itself in a suitable environment such as the epithelial surface of the intestine. The genes encoding the structural and assembly components of the TCP are located on a pathogenicity island known as the *V. cholerae* pathogenicity island (VPI)[8]. All strains of *V. cholerae* that can cause epidemic cholera contain a VPI, and it is thought to be transferred between strains in the environment. Certain features of the VPI and its chromosomal location suggest that this genetic element might be encoded by a bacteriophage[1,8,9].

Karaolis and colleagues[1] now show that the VPI is, indeed, a filamentous bacteriophage. Termed the VPI phage (VPIΦ), it can transmit itself between certain strains of *V. cholerae*, and it carries ssDNA in a similar way to CTXΦ. The protein that surrounds the DNA (the coat protein) is TcpA, a finding that has several astounding implications. First and foremost, it implies that the same structure may be both a colonization pilus and a bacteriophage particle. The authors propose that the bacteriophage can be formed and bud off from the bacterium while acting as a colonization pilus. If this is true, it indicates that the VPIΦ is the receptor for yet another phage — the CTXΦ (Fig. 1). But it is a mystery how an infectious phage particle, which must be released from the bacterial cell to infect another cell, can also act as a colonization factor and a phage receptor.

One possibility is that some of the TcpA produced by the bacterium serves one func-

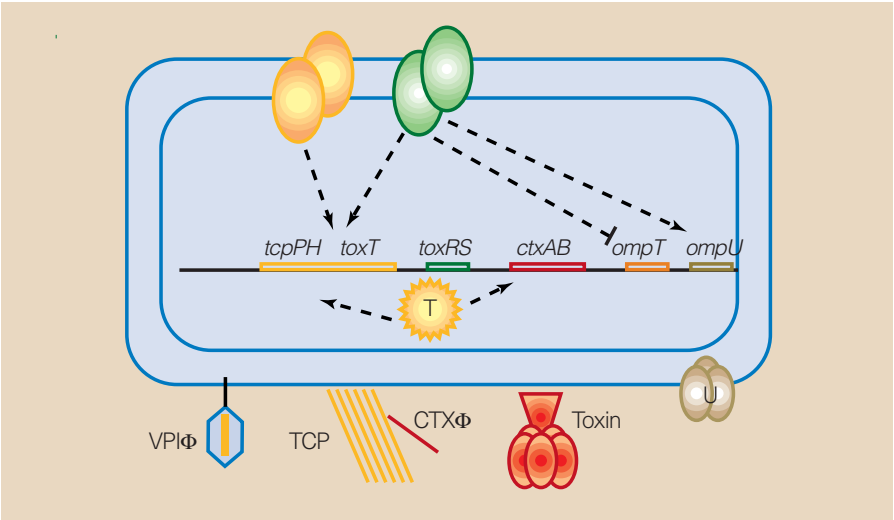

Figure 1 **Regulation of virulence genes in pathogenic *Vibrio cholerae*. The *V. cholerae* pathogenicity island phage (VPIΦ) interacts with a recipient *V. cholerae* cell, resulting in infection and insertion of VPIΦ DNA into the bacterial chromosome. This allows production of the toxin co-regulated pili (TCP), which, in turn, allows infection by the cholera-toxin phage (CTXΦ). The bacterium now has a full complement of virulence genes. Their expression is controlled by complex interactions between regulators encoded within the ancestral chromosome and those encoded on the newly acquired genetic elements. For example, the *toxR* gene product activates the expression of other genes encoding proteins in the bacterium's outer membrane (such as *ompU* in *V. cholerae*). In concert with the *tcpPH* genes (which are encoded by the VPI), *toxR* also activates expression of the VPI-encoded regulatory *toxT* gene. The ToxT protein (T) is required for expression of VPI genes, such as the *tcp* genes and the *ctx* operon of the CTXΦ, but it does not regulate expression of *ompU*[7,11].**