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# First catch your hare\*: the design and synthesis of frustrated magnets

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## Abstract

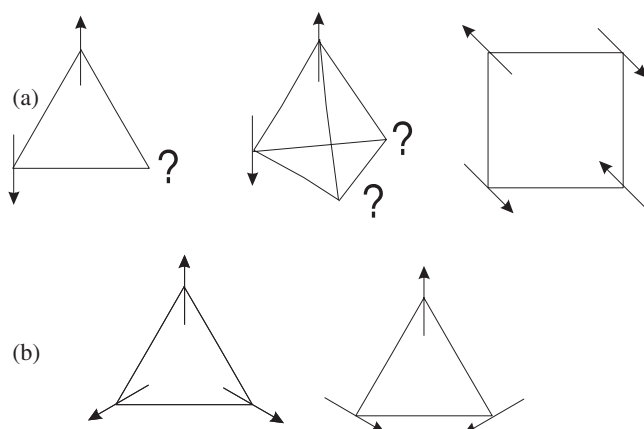
A major constraint on experimental studies of geometrically frustrated magnets (GFMs) is the availability of suitable samples that provide tangible models to inspire or test theory. Most model GFMs studied to date have been ionic compounds, for which simple models of sphere packing predict an abundance of frustrated motifs—triangular plaquettes within close-packed layers, and nets of tetrahedra in three dimensions. The various frustrated topologies that arise naturally in such systems when they are decorated with moments and exchange interactions are reviewed. An alternative approach to the design of GFMs is to build networks of magnetic species from building blocks whose geometry or valence electron configuration lead to a strong preference for a particular connectivity. This strategy may be used to build relatively dense, mainly covalently bound networks of atoms or small molecules, or more open networks in which the building blocks are larger units. Most of the applications of this type of material have been in the field of catalysis so far, but they also present new opportunities to provide GFMs with rare or new lattice topologies.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction: geometrically frustrated magnets

'Frustration' as a concept in condensed matter science is most commonly [1–7]—though not exclusively [7, 8]—associated with magnetic systems. It is generally accepted that the term was first used in this context in relation to spin glasses [9] in which magnetic atoms are distributed randomly throughout a metallic matrix, leading to random, competing exchange interactions. It is impossible to satisfy all pair-wise interactions in this type of system simultaneously, with the consequence that the mean energy scale of the magnetic interactions is reduced, and there are many nearly degenerate ground state spin configurations. However, these

\* A phrase commonly quoted from the literature of cooking, meaning that before one prepares a dish, one must have the raw materials. It is also a lesson in reading the literature carefully: it does not actually occur in the text to which it is most commonly attributed [134].



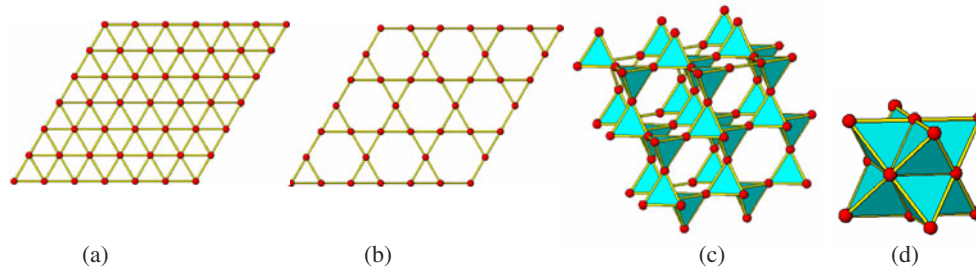
**Figure 1.** Frustrated and unfrustrated plaquettes. (a) Ising spins on a triangular, tetrahedral or square plaquette; (b)  $XY$  spins in lowest energy configurations on a triangular antiferromagnetic plaquette.

characteristic features—a lowered energy scale, and a macroscopic degeneracy (that is, of the order of the number of local degrees of freedom)—may also arise in systems in which the magnetic atoms sit on *regular* lattices, coupling through uniform exchange interactions. Here the frustration is a consequence of particular geometries of exchange pathways which prevent all pair-wise interactions from being satisfied simultaneously. Such systems are called geometrically frustrated magnets (GFM), and are most simply illustrated with regular lattices of atomic moments or spins coupled antiferromagnetically to their nearest neighbours; this has the added attraction of being a good first approximation to most insulating GFMs [10].

Figure 1(a) displays building blocks, or ‘plaquettes’ of spins found in many simple lattices: the triangular plaquette in two dimensions, and the tetrahedron in three, have geometries that prevent simultaneous satisfaction of all constituent pair-wise interactions, and for Ising spins the ground state is multiply degenerate; in contrast, the square plaquette has just one ground state whose energy is equal to the sum of the isolated pair-wise interactions. For spins with more than one degree of freedom—the  $XY$  and Heisenberg cases—we also find frustration for triangular and tetrahedral plaquettes, though the degeneracy may be different from the Ising case. For example, for  $XY$  spins on the triangular lattice, the compromise reached by competing pair-wise interactions is one of the two  $120^\circ$  arrangements shown in figure 1(b).

When the frustrated building blocks are connected to form infinite lattices in two or three dimensions, the degeneracy depends on the manner in which they are connected, and the number of degrees of freedom per spin. If triangular plaquettes are connected through every edge to their neighbours, the triangular lattice (figure 2(a)) is formed; for Ising spins the degeneracy of the lattice is macroscopic, that is, it scales with the number of sites on the lattice [11, 12]; while for  $XY$  or Heisenberg spins the system may find a doubly-degenerate ground state with two different arrangements of staggered chirality (as in figure 1(b)) on neighbouring plaquettes. However, when the triangles are connected through vertices to form the Kagome lattice (figure 2(b)) there is macroscopic degeneracy regardless of the number of spin degrees of freedom.

The most extensively studied three-dimensional GFM is the so-called pyrochlore lattice which contains a three-dimensional net of vertex-sharing tetrahedra (figure 2(c)), while the face-centred cubic (fcc) lattice may be regarded as a network of edge-sharing tetrahedra (figure 2(d)). The pyrochlore lattice [13, 14] also possesses macroscopic degeneracy,



**Figure 2.** Geometrically frustrated lattices of antiferromagnetic bonds: (a) triangular, (b) Kagome, (c) pyrochlore and (d) fcc lattices.

and presents very unconventional physics, both for the nearest-neighbour antiferromagnetic case [15–24], and for the ferromagnetic case when there is a strong easy-axis (Ising) anisotropy in the  $\langle 111 \rangle$  direction [13, 25–27].

The degeneracy, or number  $D$  of degrees of freedom, of the ground state may be estimated by a Maxwellian counting argument [28–31]:  $D = F - K$ , where  $F$  is the number of degrees of freedom of the entire system, and  $K$  the number of constraints that must be imposed to keep it in the ground state. The result for a lattice comprising  $N$  building blocks (for instance triangles or tetrahedra) of  $q$  sites which are common to  $b$  of the building blocks and occupied by spins which individually have  $n$  degrees of freedom is given by  $D/N = [q(n - 1)/b - n]$ . For Heisenberg spins, the pyrochlore lattice ( $q = 4$ ,  $b = 2$ ) has fewer constraints than there are total degrees of freedom, so we say that it is *underconstrained* ( $D/N = 1$ ); in contrast, the fcc lattice ( $q = 4$ ,  $b = 8$ ) with  $D/N = -2$  is *not* underconstrained, and does not have a macroscopically degenerate ground state. In two dimensions the Kagome ( $q = 3$ ,  $b = 2$ ) and triangular ( $q = 3$ ,  $b = 6$ ) lattices have  $D/N = 0$  and  $-2$  respectively, so the Kagome lattice is a marginal case, while the triangular lattice does not possess macroscopic degeneracy.

Of course lattices may also be constructed in which frustration arises from competition between nearest and further neighbour exchange interactions. The square plaquette with nearest neighbour (nn) antiferromagnetic exchange in figure 1(a) becomes frustrated if next-nearest neighbour (nnn) antiferromagnetic exchange is introduced: this is the classic  $J_1$ – $J_2$  model. However, it is much harder to find real materials to model such systems where a particular ratio of nn/nnn exchange strength is required [32, 33]—though the use of pressure to tune collective behaviour, noted in section 5, may offer some degree of control.

The collective magnetic properties of underconstrained GFMs are extraordinarily sensitive to perturbations to the idealized cases we have considered so far: single-ion anisotropy, dipolar interactions, deviations from scalar, Heisenberg exchange, further neighbour superexchange, and impurities or inhomogeneities in the sites or bonds of the lattice can all transform the favoured ground states, and shift the spectral weight of the excitations. Thermal fluctuations may also play a role in selecting ground states, favouring those that have a higher density of states of lower-energy fluctuations, a process known as ‘order by disorder’ [34]. When the spin is small, quantum fluctuations may be significant too. For unfrustrated lattices, classical ground states are still expected, albeit with reduced ordered moments. Frustration destabilizes such states further and may lead to the formation of a variety of more exotic spin states, based on superpositions of states composed of combinations of spin singlets. This form of composite state—sometimes called a resonating valence bond (RVB) state—is likely to have a spin-liquid character for  $S = 1/2$  on Kagome and pyrochlore lattices [35–45].

All of this interest in magnetic frustration, and the role it may play in influencing other collective phenomena, has stimulated the search for materials that model GFMs. The most

sought-after model systems have mainly been those with the simplest lattices, for which theory may be developed most readily and with greatest accuracy: model triangular, Kagome and pyrochlore magnets have provided the main focus for such work. In many cases appropriate materials were already known—either as synthetic or natural substances [46]—or could be adapted, for example by substitution of metal ions to produce different spins. However, there are still many examples of interesting model magnetic lattices that have not yet been realized, or for which current approximations are so distorted compared to the idealized model that there is doubt about their validity. So, in relation to the search for quantum spin liquids, there are examples of  $S = 1/2$  Heisenberg triangular antiferromagnets, but they are all significantly distorted [47–50]; there are also examples of  $S = 1/2$  and 1 on Kagome lattices, but they either suffer from structural distortions, or pose significant problems for the preparation of samples suitable for the most incisive measurement of spin correlations, through neutron scattering [51–58]. There is also an emerging need to place specific orbitally degenerate ions on particular lattices. Such species are prone to Jahn–Teller distortions, and the associated orbital degrees of freedom may interact with each other and the spin degrees of freedom to produce a rich variety of ordered or disordered spin and orbital structures [59–62]. The orbital contribution to co-operative magnetic effects is particularly significant when it involves a degeneracy in the most strongly antibonding orbitals associated with the magnetic centres—for which the electron–phonon coupling is strongest. For octahedral co-ordination of transition metal ions, we anticipate the effect to be most distinct for degeneracy in the  $e_g$  orbitals, which includes high-spin  $d^4$  ( $\text{Cr}^{2+}$ ,  $\text{Mn}^{4+}$ ), low-spin  $d^7$  ( $\text{Ni}^{3+}$ ), and  $d^9$  ( $\text{Cu}^{2+}$ ) configurations. Where such centres are distributed on a GFM, the degenerate orbitals are likely to be strongly disordered.

Clearly it is desirable not only to find examples of these particular models, but also to have methods to synthesize or search for further model systems. Here we describe the way in which materials with particular arrays of magnetic ions may be designed, and for insulating materials this often also defines the topology of the strongest exchange pathways. To provide a focus for this we will mainly consider ways of creating triangular, Kagome and pyrochlore lattices, though of course many of the principles extend to many more lattices. We divide the approach into methods most appropriate for insulators with different types of bonding. The structure of ionic materials, held together mainly by electrostatic interactions, may be rationalized with some success by sphere-packing models, described in section 2. The majority of model magnetic materials are compounds containing transition metals, M, and one or more highly electronegative element, X, and here the structure may be commonly viewed in terms of  $\text{MX}_n$  co-ordination polyhedra linked in a variety of ways; we describe this way of visualizing structures in section 3. In section 4 we consider structures in terms of the topology of a network of bonds, an approach that is commonly used for networks of covalently bound atoms. However, a recent development in materials design is to build such networks from structural units that may be much larger than individual atoms, and we consider the opportunities that this may offer in the search for new model magnetic systems.

There are classes of material which provide, or have the potential to provide, GFMs, which we will not consider here. Metallic alloys may combine magnetic frustration with itinerant electronic behaviour, and the consequences of coupling two types of degree of freedom may be fascinating physics [63–66]. However, the long-range oscillatory nature of the exchange in such materials means that it is more difficult to relate the crystal lattice to a relatively simple lattice of exchange interactions. We will also neglect molecular crystals in which the constituent molecules are not linked by primary covalent bonds, but rather by weaker interactions such as hydrogen bonds or  $\pi$ – $\pi$  interactions. In some cases one can predict with some confidence the likely way in which the individual molecules will be arranged in the crystal structure, and the likely nature of any significant electronic interactions—as well as

magnetic interactions in the case of molecules that contain unpaired electrons, either because they contain a paramagnetic metal centre, or because they are wholly organic radical species. Many crystals formed from planar molecules with delocalized  $\pi$ -electron systems form stacks of these units, and the principal type of electronic interaction is along the axis of the stack. However, when such structural features are absent, it is generally very difficult to predict the relationship between the structure of the individual molecules, and the network of the most significant exchange interactions. Finally, GFMs may be formed when thin films of atoms with nuclear moments are condensed on a suitable substrate:  $^3\text{He}$  possesses a nuclear spin  $1/2$  and is known to form a number of layered triangular and Kagome lattices when it is condensed onto a graphite surface, depending on the coverage of the surface; this system is particularly fascinating on account of the multiple-spin exchange, involving more than two moments, and provides fundamental insights into quantum magnetism [67–69].

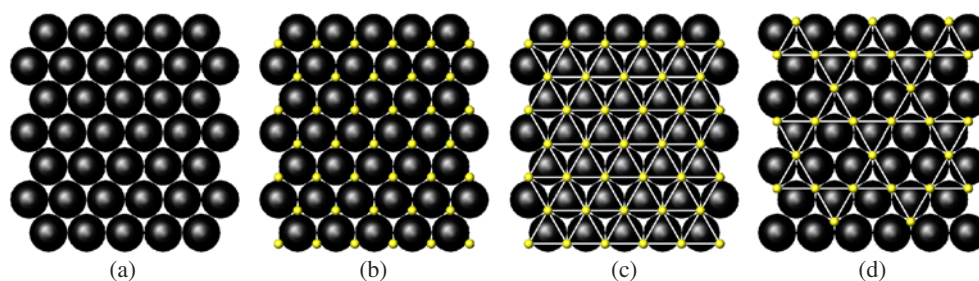
## 2. Structural models for ionic materials: sphere packing

Compounds formed between electropositive metals and highly electronegative elements have a significantly ionic character, and the dominant contribution to their lattice enthalpy arises from Coulombic interactions. In such cases structures may be predicted with some success on the basis of closest packing of spheres whose radii correspond to those of constituent ions [70, 71]. The anions are usually larger than the cations (for  $\text{O}^{2-}$  and  $\text{F}^-$ , the ionic radii are 1.35–1.42 and 1.285–1.33 Å depending on the co-ordination of anions about cations, whereas typical radii for divalent first-row transition metal ions in oxides and fluorides are 0.6–1.0 Å [72–74]), so the basis for such structures is often closest packed arrays of one type of sphere (anions), with smaller spheres (cations) placed in the interstices. This leads to a host (anion) structure based on triangular layers which may be stacked in a variety of ways: closest packing corresponds to structures in which each atom in a closest packed layer (1) touches three atoms in the layer above (2), and three in the layer (3) below, giving a total of 12 nearest neighbours. There are two distinct ways in which layers (2) or (3) may nestle with (1) to be closest-packed and retain translational symmetry, so we can define up to three types of layer, A, B and C, which differ by translations in the plane of the layer. Common stacking sequences are . . . ABCABC . . . (which gives a cubic (cp) lattice), and . . . ABABAB . . . (which gives a hexagonal (hp) lattice). However, non-closest packing sequences, in which adjacent layers have the same label, are also common, and point to the presence of significant non-ionic contributions to the bonding.

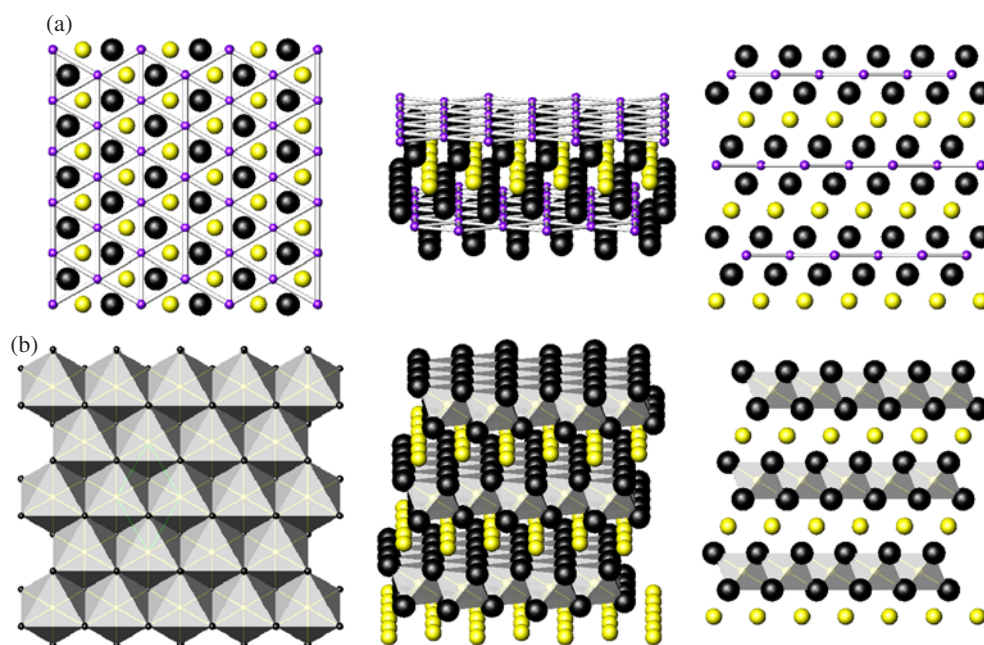
For magnetic materials, the lattice of interest has the cations at the vertices, and the bonds correspond to the significant exchange pathways. For high symmetry structures built from closest-nestling of layers there are two common locations for the cations within the anion host: six co-ordinate (octahedral) and four co-ordinate (tetrahedral) sites, both of which describe a triangular lattice; the former case is illustrated in figure 3. For non-closest nestling of layers (e.g. . . . AA . . .), the interstices have trigonal prismatic co-ordination, and these sites describe a honeycomb lattice (though of course the way in which these sites interact most effectively will depend on the precise exchange pathways, and it is quite possible there will be significant further-neighbour exchange).

In principle there are a number of ways in which the pattern of interstitial sites may be manipulated to produce different magnetic lattices: (i) change the occupancy of interstitial sites from layer to layer; (ii) alter the occupancy of the interstitial sites for a given layer. Let us consider how one might produce isolated triangular and Kagome lattices by manipulating denser magnetic lattices in these two ways.

- (i) If we replace every interstitial magnetic atom in alternate layers either by a diamagnetic atom or a vacancy, we increase the separation between triangular lattices of the magnetic



**Figure 3.** (a) The closest packing of spheres in a layer; (b) the position of the octahedrally coordinated interstitial sites between closest-nestled closest-packed layers; (c) the triangular lattice of interstitial sites; (d) Kagome lattice derived from the triangular lattice by systematic removal of  $1/4$  of the magnetic sites.



**Figure 4.** Ordered NaCl-type superstructures found in  $\text{NaTiO}_2$  and many ternary oxides depicted (a) with a sphere packing model, with emphasis placed on the lattice of magnetic sites and (b) as layers of edge-sharing metal–oxygen octahedra. In both cases the left- and right-hand figures show the view respectively parallel and perpendicular to the magnetic layers, and the central figures are intermediate views.

atoms. The first approach is only likely to work if there is a clear difference between the two types of cation, for example size or charge, and a key example of such a material is provided by many ternary oxides and chalcogenides of formula  $\text{MM}'\text{O}_2$ , where M and M' are uni- and trivalent species respectively, and X is the divalent anion (figure 4).  $\text{NaTiO}_2$  and  $\text{LiNiO}_2$  have structures based on a cp array of  $\text{O}^{2-}$ , with alternate layers of interstices filled with the univalent ion or the transition metal ion, and have been studied as model triangular  $S = 1/2$  antiferromagnets [75] (though it should be noted that both materials show significant distortion from the idealized structure [49, 50]. If the two metal ions are not sufficiently distinct, statistical disorder may occur—as is common in  $\text{LiNiO}_2$  [6].

The mineral delafossite,  $\text{CuFeO}_2$ , has a similar structure to  $\text{NaTiO}_2$ , though the nesting of closest-packed  $\text{O}^{2-}$  layers is slightly different; it too provides a rich source of model triangular magnets, as well as dilute Kagome lattices when oxidized [8, 76, 77]. The strategy of replacing interstitial magnetic centres in alternating layers with vacancies is realized in materials with the so-called  $\text{Cd}(\text{OH})_2$  structure (sometimes called the  $\text{CdI}_2$  structure). This is based on a hp sequence of closest-packed layers of  $\text{O}^{2-}$  with the octahedral interstitial sites of alternate layers occupied by  $\text{Cd}^{2+}$ . Many transition metal hydroxides and heavier halides adopt this structure and are also studied as model triangular antiferromagnets [78, 79].

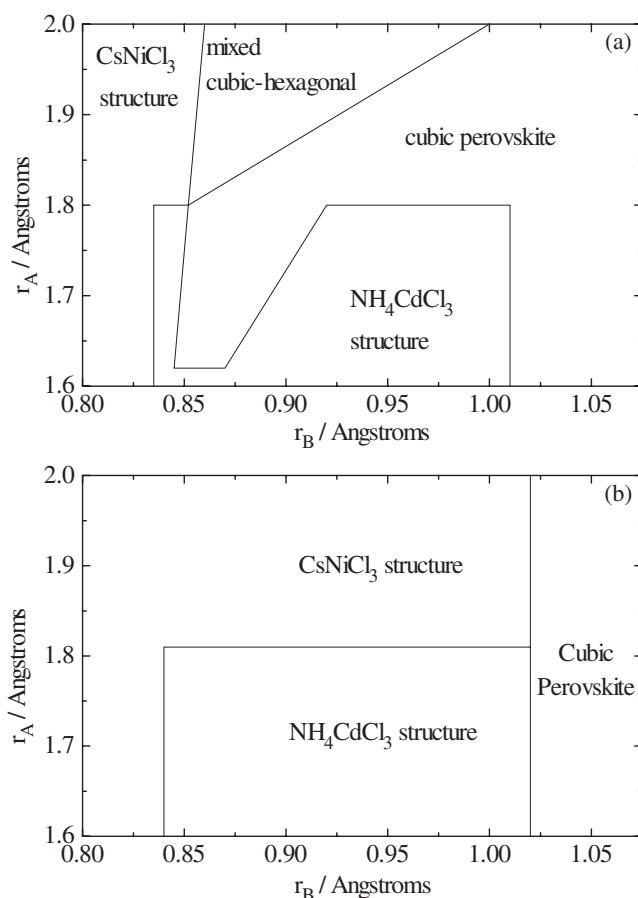
- (ii) If the interstitial magnetic atoms within a layer are replaced by other species, a variety of sparser magnetic lattices may be produced. Figure 3(d) depicts a triangular array in which 1/4 of the sites have been systematically removed, or replaced by a diamagnetic ion to leave a Kagome lattice. This process may be illustrated by the material  $\text{Na}_2\text{Mn}_3\text{Cl}_8$  [80]: if one imagines starting with  $\text{MnCl}_2$ , and removing 1/4 of the  $\text{Mn}^{2+}$  ions, one would produce layers of composition  $\text{Mn}_3\text{Cl}_8^{2-}$  which requires a complementary 2 units of positive charge dispersed in the structure (in the case of  $\text{Na}_2\text{Mn}_3\text{Cl}_8$  this takes the form of  $\text{Na}^+$  ions between the layers).

The examples we have considered so far simply use the ionic model and principles of sphere packing to visualize or classify the structure: in practice it is often either difficult, or impossible, to predict precisely which structures will form for a given set of elements using these principles. That is not to say that the ionic model has no role to play in narrowing the search for materials with a particular lattice—and in particular in pointing to new examples of model magnetic materials. It is often possible to map out the occurrence of different structure types for metal compounds of a given composition in terms of the ionic radii of the constituent ions. The empirical diagrams that result are sometimes called structure-field maps [81], and they may provide a good starting point to predict the structure of ionic materials formed between ions with particular radii, and in some cases also to predict the likely response of the structural stability to applied pressure. Figure 5 gives one example of a structure-field map for  $\text{ABX}_3$  halides [82], where A is a univalent cation, B is a divalent ion (typically of a first-row transition metal), and X is a halide ion ( $\text{Cl}^-$  and  $\text{Br}^-$  in this case). Depending on the size of  $\text{A}^+$  and  $\text{B}^{2+}$ , a variety of polytypes are found, including hexagonal perovskites with the  $\text{CsNiCl}_3$  structure, and these have provided a very rich source both of one-dimensional model magnets, and also of triangular antiferromagnets [79, 83, 84].

### 3. Coupling of polyhedra

An alternative method of visualizing structures that is particularly common for transition metal compounds, and which recognizes the prevalence of particular local requirements for bonding, is to construct lattices by linking co-ordination polyhedra, and there are well-established rules (commonly called the Pauling rules) that allow us to predict with some success what the prevalent polyhedra should be, and how they should be connected [70, 71, 85–88]. The single sheet of fully edge-sharing  $\text{MO}_6^{(4-n)-}$  octahedra (where ‘ $n$ ’ is the formal charge on the metal ion, and the layer itself has stoichiometry  $\text{MO}_2^{(4-n)-}$ ) observed in many layered oxides, and illustrated for the case of  $\text{NaTiO}_2$  in figure 4(b), provides a good template for constructing triangular and Kagome lattices. The ordered depletion of the layers of metal atoms to produce Kagome and orthorhombic derivatives that we described in the previous section is recast in terms of co-ordination polyhedra in figure 6. Such layers may be linked in a variety of ways in real materials. In  $\text{NaTiO}_2$ ,  $\text{Na}^+$  balances the ‘ $\text{TiO}_2^-$ ’ sheets to give charge neutrality.

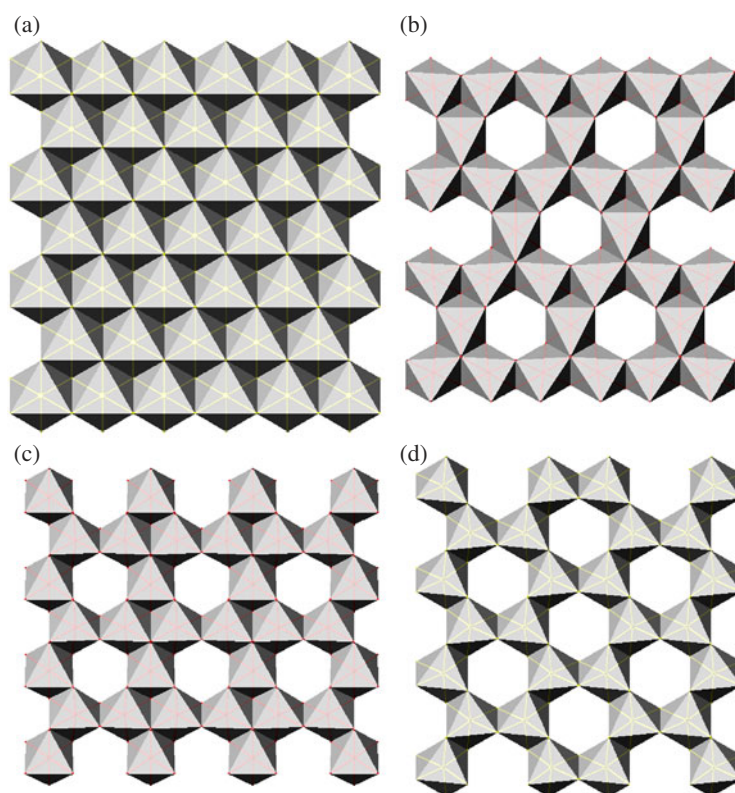




**Figure 5.** A structure-field map for ABX<sub>3</sub> halides, where A is a univalent cation, B is a divalent ion—typically of a first-row transition metal, and X is a halide ion —Cl<sup>−</sup> and Br<sup>−</sup> for (a) and (b) respectively [82].

Much greater isolation of the layers is found in layered transition metal hydroxides such as Cu<sub>2</sub>(OH)<sub>3</sub>X, where X is an anion such as NO<sub>3</sub><sup>−</sup> that may be exchanged by a much bulkier entity such as an alkanecarboxylate molecule, prising the layers apart [89, 90]. Other construction schemes are also displayed in figure 7: insertion of Ca<sup>2+</sup> between the (non-magnetic) Pt<sub>3</sub>O<sub>4</sub><sup>2−</sup> Kagome layers in CaPt<sub>3</sub>O<sub>4</sub> [91], and pyrovanadate units (V<sub>2</sub>O<sub>7</sub><sup>4−</sup>) between the Cu<sub>3</sub>(OH)<sub>2</sub><sup>4+</sup> Kagome layers in the mineral volborthite, Cu<sub>3</sub>V<sub>2</sub>O<sub>7</sub>(OH)<sub>2</sub>·2H<sub>2</sub>O [54, 55, 58, 92].

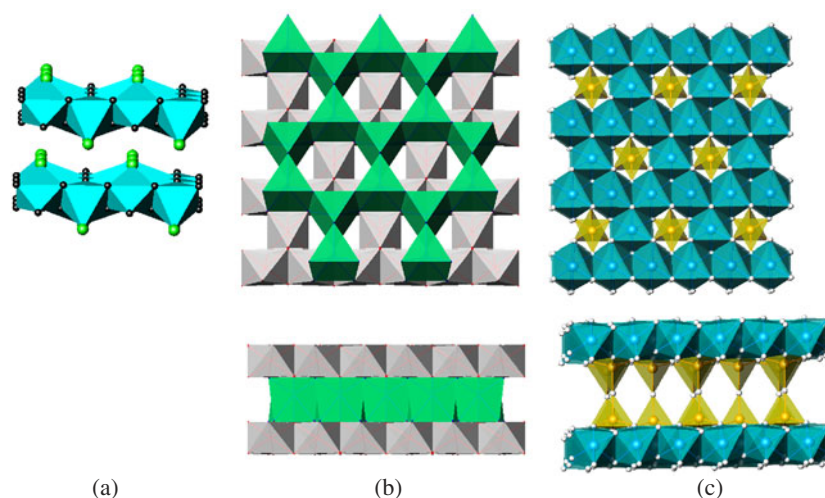
An alternative method of building a Kagome lattice is through *vertex*-sharing of octahedra, as displayed in figure 8. This is a very common structural element in solid oxides [88, 93] and fluorides, and indeed much of the earliest systematic work in developing model frustrated systems was based on fluorides [94]. Figure 9(a) displays such layers, and the way in which they are interconnected in the hexagonal tungsten bronze (HTB) structure for which the archetype is A<sub>x</sub>WO<sub>3</sub> (A = K, Rb, Ti, Cs, In) [95], but which is also displayed by one form of FeF<sub>3</sub> [96] (figure 8(a)). In that case, the Kagome layers are not particularly well isolated, but they may be separated by layers of diamagnetic ions as observed in the series A<sub>3</sub>A'Mn<sub>3</sub>F<sub>12</sub> (A = Rb, Cs; A' = Li, Na, K) [97], and illustrated in figure 8(b). One oxide that is constructed from vertex-sharing octahedra, and which is part of an extensive family of compounds, is the mineral



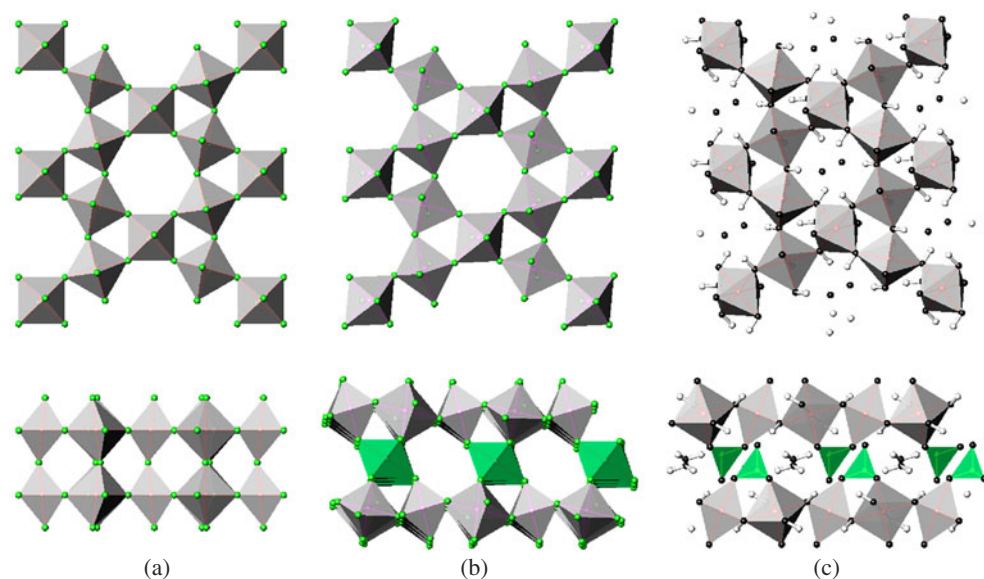
**Figure 6.** The construction of sparser two-dimensional lattices through systematic removal of magnetic atoms from a triangular lattice (a). The Kagome lattice (b) is obtained by removing 1/4 of the atoms, while the unfrustrated rectangular (orthorhombic) lattice (c) has the same coverage but a different pattern of removal. (d) is the unfrustrated honeycomb lattice obtained through systematic removal of 1/3 of the metal centres.

jarosite,  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ , depicted in figure 8(c) [98–102]: isomorphs exist with iron substituted by chromium ( $S = 3/2$ ) [103] or vanadium ( $S = 1$ —though in this case the material has nn ferromagnetic exchange in the Kagome layers) [104–106]. The jarosites are arguably the most extensively studied model Kagome systems that relate closely to the simple systems for which theory has been developed. However, they do suffer from structural disorder, and most natural and synthetic samples have incomplete coverage of the magnetic lattice; they are also very difficult to prepare as crystals suitable for the most incisive inelastic neutron scattering measurements, which typically requires samples whose size is at least  $10 \text{ mm}^3$  (though natural crystals at least an order of magnitude larger than this are readily available). These shortcomings have been rectified to some extent with the development of a redox-based hydrothermal technique that releases the trivalent metal ions into solution very slowly, with the result that the product has negligible structural disorder, and forms crystals sufficiently large for single-crystal x-ray diffraction [102]. This type of development is particularly significant for model GFMs because their collective properties are so sensitive to minor perturbations, and it dangerous to infer the inherent behaviour of a pure model system from measurements on even slightly disrupted derivatives.

The Kagome layers in HTB may be also connected in such a way as to produce three-dimensional frustrated lattices. In the case of  $\text{FeF}_3$ , there is another form in which the layers,

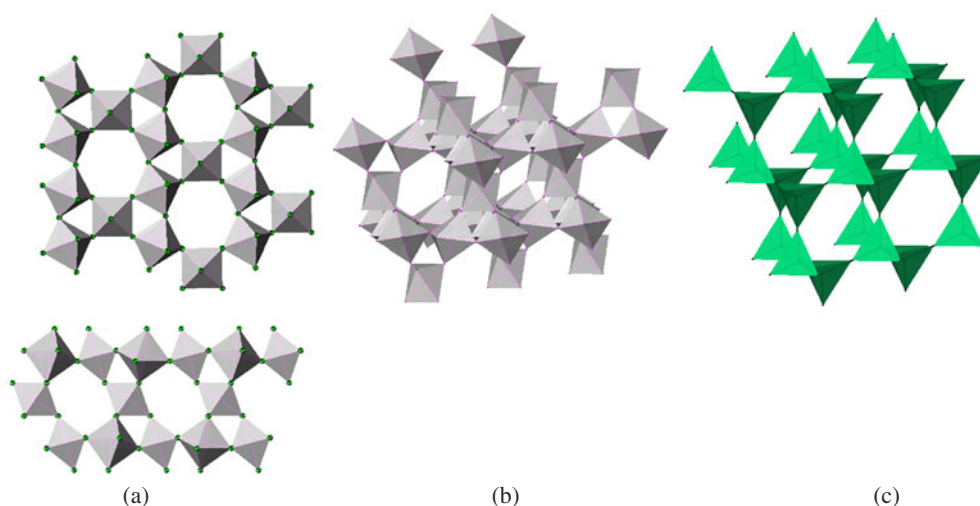


**Figure 7.** Separating frustrated layers in (a)  $\text{Cu}_2(\text{OH})_3\text{X}$ , (b)  $\text{Ca}_2\text{Pt}_3\text{O}_4^{2-}$ , and (c) volborthite ( $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ ).



**Figure 8.** The construction of Kagome lattices through vertex-sharing of octahedra: (a) hexagonal tungsten bronze structure, exemplified by  $\text{FeF}_3$ ; (b)  $\text{A}_3\text{A}'\text{Mn}_3\text{F}_{12}$  ( $\text{A} = \text{Rb}, \text{Cs}$ ;  $\text{A}' = \text{Li}, \text{Na}, \text{K}$ ); (c) the jarosite family of minerals exemplified by  $\text{KFe}_3(\text{SO}_4)_3(\text{OH})_6$ . All structures are viewed from directions perpendicular (top row) and parallel (bottom row) to the Kagome layers.

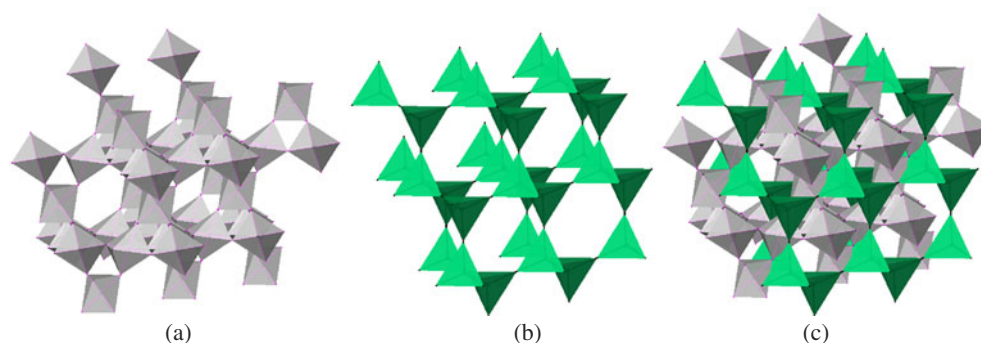
displayed again in figure 9, are connected not through apical fluorine atoms to an identical layer below, but rather through an  $\text{FeF}_6^{3-}$  octahedron that caps each triangle of iron fluoride octahedra in the Kagome layers. If this process is extended in the direction perpendicular to the layers (figures 9(a)–(c)), a pyrochlore lattice of magnetic centres is produced. This is also common among oxides: figure 10 shows a general scheme of constructing such a lattice from Kagome layers of composition  $\text{BO}_3$ ; the figure indicates that the lattice also contains voids that



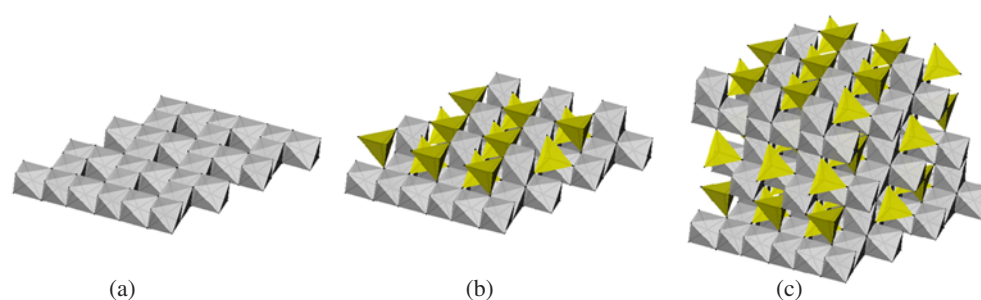
**Figure 9.** The construction of a pyrochlore network from hexagonal tungsten bronze (HTB) layers. (a) A pair of HTB layers, viewed from above (top) and from a direction parallel to the layers (bottom), showing how the layers are linked through additional octahedra that cap each triplet of vertex-sharing octahedra in the HTB layers; (b) depicts this process from a three-dimensional perspective while (c) picks out the lattice of the centres of the octahedra, which has a pyrochlore structure.

may accommodate additional ions A, and perhaps additional oxygen, to produce  $A_{1+x}B_2O_{6+y}$ . The stoichiometric case,  $A_2B_2O_7$ , is exemplified by  $Ln_2B_2O_7$ , (Ln is a trivalent lanthanide, and B is a tetravalent ion such as T, Sm, Zr) [14, 107]. In this case both the A and the B cations describe a pyrochlore lattice, sitting at sites 16d and 16c respectively of the  $Fd\bar{3}m$  space group. Finally, in the context of three-dimensional frustrated lattices, note should be taken of the spinel structure. The generic formula of the normal spinel is  $AB_2O_4$ , where A is a tetrahedrally co-ordinated ion, and B is octahedrally co-ordinated. The network of the  $BO_6$  octahedra is the same as that found in pyrochlore, with  $AO_4$  units dispersed throughout (figure 11). Attention was first drawn to this feature and the consequence it has for collective magnetic properties for ferrites with this structure, in which  $Fe^{3+}$  normally sits on the spinel B site [15], and materials have since been studied with a much wider range of magnetic ion at this site [108]. It should also be noted that the  $BO_6$  octahedra share edges rather than vertices, as with the pyrochlore lattice, with the consequence that further-neighbour interactions are more significant. Interest in this class of material is heightened by virtue of the fact that some members of this class of compound show itinerant electronic behaviour [109], and some are important battery materials [110]. There are also layered lattices that incorporate slabs of spinel such as magnetoplumbite ( $PbFe_{12}O_{19}$ ) isomorph  $SrCr_{12-x}Ga_xO_{19}$ ; the frustrated lattice of  $S = 3/2$  on the  $Cr^{3+}$  is best regarded as decoupled layers of pyrochlore with a thickness of two vertex-sharing tetrahedra, and was one of the earliest underconstrained systems to be studied experimentally [111–113].

In breaking the lattice down into co-ordination polyhedra, then considering ways of putting these building blocks together, has anything that has predictive value been achieved? As with sphere-packing, the answer is that it is often difficult to predict with much confidence what structure is likely to be produced for a given combination of elements: there are exceptions—classes of very well studied materials such as perovskites and their structural relatives in which structure–property relations have been extensively studied and for which semi-empirical rules



**Figure 10.** The structure of (a) oxide pyrochlores of stoichiometry  $A_2B_2O_7$ , separated into a 'host' pyrochlore network (b) of stoichiometry  $BO_3$  which can accommodate 0.5 equivalents of oxide  $A_2O$ , itself disposed as a pyrochlore network of A atoms (c).



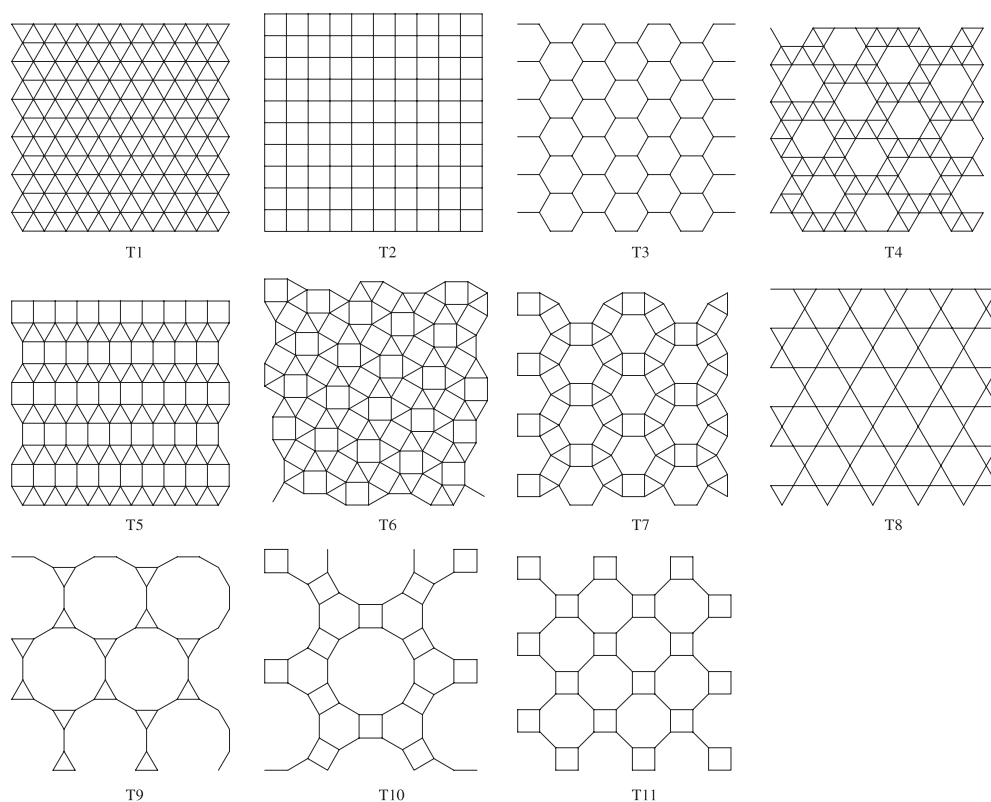
**Figure 11.** The structure of spinels of formula  $AB_2O_4$  broken down into a pyrochlore network of the centres of  $BO_6$  octahedra with  $AO_4$  tetrahedra dispersed systematically throughout. (a) depicts a single HTB layer, (b) the capping of the triplets of octahedra by single octahedra (as shown from a different angle in figures 9(a), (b) and 10(a)), and the addition of  $AO_4$  tetrahedra. Repetition of this process leads to the spinel lattice (c) in which the B atoms describe a pyrochlore lattice.

have been developed. However, even simple systems often lie close to boundaries between several different structures:  $FeF_3$  exists not only in the HTB and pyrochlore forms, but in another crystalline form (isomorphous with  $ReO_3$ ) and amorphous forms [96]. The primary role that this way of regarding crystal structures plays is in visualizing and classifying structures, and it may also point to isomorphous materials containing different metal ions on a chosen lattice.

#### 4. Networks: chemically directed design of lattice topology

The strong preferences that some atoms and molecules show for particular local co-ordination geometry complicates a simple implementation of the ionic model, but opens up another method of rationalizing and classifying lattice structures. Each such atom or molecule may provide a node or vertex in a network; conversely, if we wish to construct a particular network, one starting point might be to link together atoms or molecules that are known to favour the same local co-ordination as the nodes of the network possess.

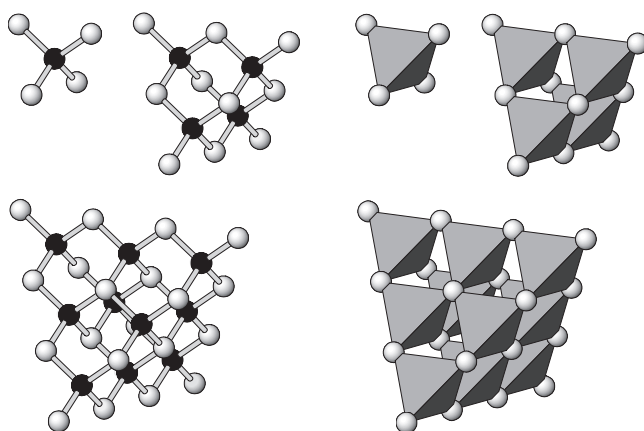
This approach is widely used in the search for new microporous materials, with pores or channels that are often large on the atomic scale, and which may also incorporate some catalytic, electronic, magnetic or optical functionality into the lattice. The methodology that



**Figure 12.** The 11 uniform Archimedean lattices: the uniform tilings T1, T2 and T3 are the triangular, square and honeycomb lattices respectively, and the tiling T8 is the Kagome lattice, but none of the others have standard names. (Figure provided courtesy of Schulenburg [45].)

is being developed could also have important implications for the way in which new model magnetic and electronic materials are sought and synthesized.

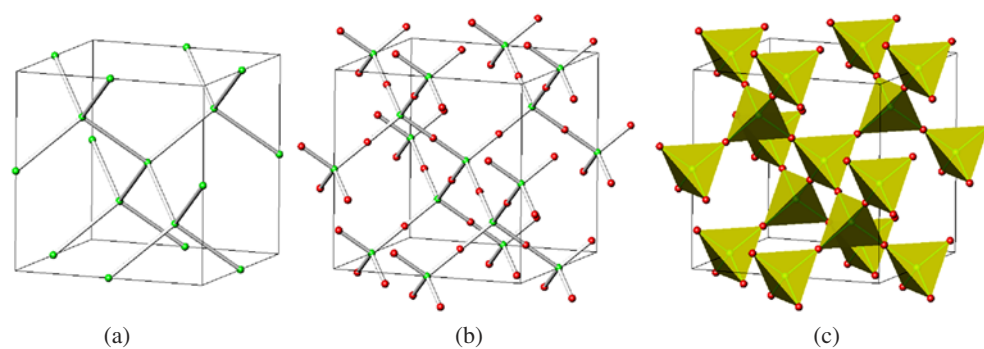
The starting point of much of this work is to consider what networks are possible, subject to various constraints on the symmetry of the nodes, lengths of bonds, and angles between those bonds [70, 114–117]. In the special cases where all these properties are equivalent we say that the network is *regular*, while if we lift the constraint on all angles being the same, we say the network is *quasi-regular*. These special cases are particularly relevant to real materials in which the constraints of translational invariance, identical bond-lengths between equivalent atoms, and preferences for particular local co-ordination geometry about an atom, or larger structural unit, are commonly present. In two dimensions there are just three regular and eight quasi-regular networks (the 11 uniform Archimedean lattices displayed in figure 12), but there are many more in three dimensions. However, it is observed that only a small subset of networks are common in real materials, most of which are regular or quasi-regular lattices with the most symmetric vertices [117]. From the point of view of designing GFMs, the feature of such nets that is of greatest interest is probably the number of bonds in closed loops in the lattice; among the most common nets in three dimensions there are very few examples with an odd number of bonds in the smaller loops in the lattice—notably the pyrochlore lattice (though of course if the lattice is bipartite, with sublattices A and B, one of the sublattices may now have an odd number of bonds in these smaller loops). Much of the work in this field has also



**Figure 13.** Tetrahedron and supertetrahedra of increasing size.

focused on nets of relatively low connectivity, because its principal aim is usually to produce open framework materials.

The simplest and conventional way to proceed from the abstract to the concrete is to consider networks built just from one or two types of atom connected directly through covalent bonds. However, the same approach may be used with more complex building blocks into which particular functionality may be incorporated; in recent years such entities have acquired the generic name ‘structural building unit’ (SBU) [118–120]. So, while tetrahedral vertices are found in covalent networks such as diamond, one can imagine the same type of vertex being provided by more complex building blocks that retain a tetrahedral shape and link only through the vertices (figure 13). This specific method of decorating a net was employed in the formation of a very open framework form of indium sulfide in which the tetrahedral vertices of the conventional dense lattice are replaced by clusters of tetrahedra such as  $\text{In}_{10}\text{S}_{10}^{10-}$  [121]. It is conceivable that this approach could be useful in developing model magnetic systems comprising nets of high spin magnetic particles, where the SBUs are high-nuclearity clusters of metal ions [122–124]. Such models might be used to explore and exploit the collective behaviour of arrays of magnetic nanoparticles, as might be used in very high density magnetic recording. At first sight it is less clear that this method has much to offer the field of GFMs, at least in terms of key current problems, where there is a demand for lattices of small spins, near the quantum limit, or an interplay between local spin and orbital degrees of freedom. However, the method need not be pushed towards the limit of large SBUs; in augmenting certain types of vertex by small frustrated polygons or polyhedra—for instance the three-connected vertex by a triangle, and a tetrahedral vertex by a tetrahedron—we produce a lattice of frustrated plaquettes, with a lower connectedness (and hence more underconstraint) than the parent lattice. In addition, the method may be used to modify known lattice types by expansion or other forms of modification of the bonds. This is illustrated schematically in figure 14 in which the bonds, C–C, of a diamond lattice are replaced by C–X–C. In this particular case we end up with the crystobalite lattice, found for that particular polymorph of  $\text{SiO}_2$ , as well as for  $\text{Cu}_2\text{O}$ , and related to the network of the  $I_c$  phase of ice; the linearly co-ordinated atom in these structures (O, Cu and H respectively) sit at the vertices of the pyrochlore lattice (figure 14(c)). In the context of model magnets, inserting a longer link between magnetic atoms at the vertices will generally lead to weaker exchange for a given character of linking group: if we insert bifunctional alkyl chains of the form  $\text{Y}(\text{CH}_2)_n\text{Y}$ , for which the terminal groups Y may co-



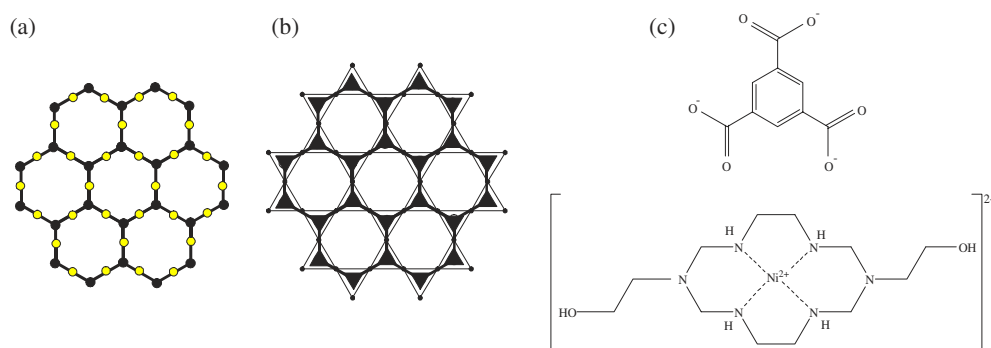
**Figure 14.** (a) The diamond network expanded in (b) through the replacement of C–C bonds by C–X–C, making the crystal structure in which X lies at the vertices of a pyrochlore lattice (c).

ordinate to magnetic ions at the vertices of the network, then it is most likely that magnetic exchange will decrease sharply as the alkyl chain length  $n$  increases; however, if we exchange a short-chain alkyl linker (for instance with  $n = 2$ ), by a longer, unsaturated or conjugated molecule such as paraphenol ( ${}^{-}\text{O}-\text{C}_6\text{H}_4-\text{O}^{-}$ ) it is conceivable that exchange will increase.

When one attempts to modify materials in this fashion, one does not always produce the desired product—particularly if long, flexible linking agents are used: in such cases kinetic and entropic factors may lead to the growth of disordered or lower-connected structures; retention of the parent structure is favoured—but by no means guaranteed—by the use of structurally rigid molecules such as aromatic homo- or heterocyclic hydrocarbons. There are circumstances when this approach might be useful in model magnetism: if one wishes to extend the experimentally accessible range of field,  $H$ , in relation to exchange,  $J$ , reduction of  $J$  augments work at high  $H$ , and provides access to a wider range of field-tuned systems. This has particular relevance to frustrated quantum systems where  $H$  may switch the system between quantum disordered and ordered states [42, 43, 125, 126]. As a network expands and the amount of free volume increases, it becomes more likely that this free space will be taken up by another, interpenetrating network, generally identical to the first [127]. Another facet of expansion that could hold considerable promise in designing new GFMs is the case in which the entity used in the expansion contains a magnetic centre, producing a magnetic lattice that is a dual of the original; an application of this method to produce a Kagome lattice is described below, and we noted above that the lattice formed by connecting the centres of the bonds of the diamond lattice is a pyrochlore lattice (figure 14(c)).

The most direct implementation of this method of directing the growth of particular lattices for model frustrated magnets is to combine rigid polydentate ligands with transition metal ions, or transition metal ion complexes that have a strong preference for a specific local co-ordination geometry. Either type of species could play the role of either a bond or a vertex in a network. Ligands that provide bonds must be at least bidentate, and possess some ability to convey magnetic exchange, and there are many examples of suitable species. Ligands that provide vertices must be at least tridentate (and, for many desirable lattices, have a three-fold symmetry axis relating the binding sites). There are many classes of molecule that may play one or both of these roles, most typically polyfunctional carboxylates, phenols, alcohols and aromatic heterocyclic molecules. Transition metal ions most commonly adopt octahedral or tetrahedral co-ordination in extended solids and complexes, with square-planar and other structural motifs less common. However, if one tries to combine a multidentate ligand with a metal centre that favours octahedral co-ordination, there are many possible ways they may be combine; for

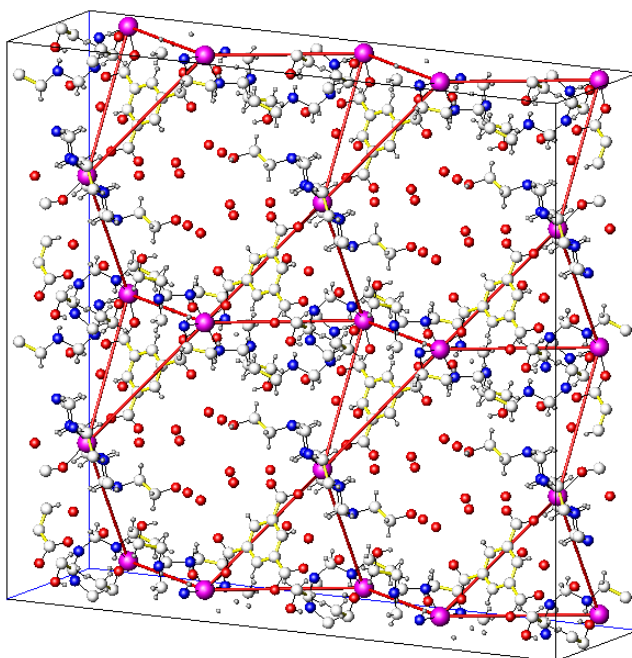




**Figure 15.** (a) The honeycomb network and (b) the Kagome dual produced by connecting the centres of its bonds. (c) Potential chemical building blocks likely to favour a Kagome lattice of magnetic centres built in this fashion. The nickel macrocycle, below, can only bind easily to two ligands and the anion, above, may easily bind to up to three cations.

instance, a single metal centre may bind to a single site on six different ligands, or to several sites on a smaller number of ligands. The process of finding out how best to direct such processes is still at an early stage, and although modelling work has been done to predict the possible networks that may form from a particular solution of SBUs [128], most of the work in this field involves searching through the many parameters that might favour a particular network by trial and error. So, for a particular metal centre and ligand, the relative proportions of reagents, and the order in which one is added to the other, may alter the growth, as might the nature of the solvent, temperature, and presence of ‘innocent’ counter ions. Further, it is sometimes found that reaction mixtures containing both potential linking ligands and metal centres yield nets of condensed metal oxide polyhedra, with the organic units bound into voids or channels in the network; although this complicates the process of prediction, it also adds greatly to the potential range of sparser lattices [129]. In order to narrow the range of structures that might form, it may therefore be desirable to impose greater constraints on the ways in which metal centres and ligands may combine. To illustrate this, consider how one might direct the growth of a Kagome lattice of exchange coupled metal ions.

The most straightforward method would be to note that the Kagome lattice is one of the 4-connected plane nets and therefore aim to use metal ions that have a propensity to bind to four ligands in an equatorial plane. However, it is not clear how one would provide a reliable mechanism for selecting the Kagome network over the square lattice—or indeed polymeric strands of metal centres in which two of the sites did not link into a network (it is conceivable that one might introduce some form of molecular template to the growing system that acts as an anchoring point for triangular clusters of metal ions, but then one risks incorporating the template into the network in an unhelpful fashion). An alternative way to view the Kagome network is to note its relation to the honeycomb network (figure 15(a)): the centres of the bonds of the honeycomb network are the vertices of a Kagome network (figure 15(b)). This could be realized by inserting metal ions between tridentate ligands. To optimize the chance of doing this, one would choose metal ions that only had the capacity to bind to two ligands at 180° to each other—as found in metal ions that are already co-ordinated in a planar, macrocyclic molecule. Figure 15(c) displays examples of such building blocks: the compound formed by combining such species (specifically the Ni<sup>2+</sup> macrocycle, Ni(C<sub>12</sub>H<sub>30</sub>N<sub>6</sub>O<sub>2</sub>, with benzene tricarboxylic acid) under certain conditions has the distorted Kagome network of  $S = 1$  centres displayed in figure 16.



**Figure 16.** A model  $S = 1$  Kagome antiferromagnet based on the scheme depicted in figure 15 [52].

## 5. Conclusions

Chemists and materials scientists will continue to use their intuition, backed to some extent by models based on sphere packing and linking of co-ordination polyhedra, to predict and produce GFMs. The most significant recent development in the methods of producing new lattices the linking of SBUs, and has mainly been directed at the search for new microporous or framework materials. However, the same principles may be applied to the search for new magnetic networks. It is likely that such materials will have relatively open structures, which are more likely to show magnetic underconstraint, and they are also more likely to show weaker exchange interactions, which may be desirable for model systems to be tuned though the application of a magnetic field. There is much to be explored in this field, particularly the factors that control the formation of particular lattice geometries, and the potential for different ligands or molecules to mediate exchange. Finally, model systems may be tuned continuously and cleanly through the application of external fields. The role of  $H$  in selecting ground states, particularly in quantum GFMs, has been noted, and is widely used because it is also widely available. Less common is the application of pressure to tune structure and through it magnetic exchange. The particular sensitivity of superexchange to pressure is widely known, and dependences of the form  $J \sim r^{-10}$  have been reported for particular insulators [130, 131], opening the door not only to stronger nn exchange, but variable ratios of nn to nnn interactions (one can imagine, for example, tuning the ratio  $J_1/J_2$  in the  $J_1$ – $J_2$  model, given the right model system). However, such studies are still non-routine, and to achieve their optimum potential require parallel measurements of structure and magnetic response under pressure; this in turn requires improvements to the sensitivity and pressure range of magnetization or susceptibility measurements relative to what is currently available [132, 133]. A key to success in this field may therefore be found in strong partnerships between physicists, chemists and engineers who can design, synthesize, manipulate and measure GFMs to reveal their fascinating properties.

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