Chemistry and the synthesis of novel materials*

Peter Day

Davy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London W1X 4BS, UK

Abstract: The significant feature of materials science is that it deals with matter in bulk, and hence with properties which are those of the aggregate, not just the sum of the constituents. That has made it harder for chemists than for physicists to comprehend structure–property relations, because chemists instinctively view solids as built from individual atoms or molecules. But involvement of chemists in materials science has brought much greater variety and complexity in the range of substances being prepared and studied, both with respect to structures and properties. This lecture introduces some of the physical properties that have been of interest recently to chemists, and some of the novel types of compound that are being synthesised. The emphasis is on superconductors and other materials made from molecular components.

INTRODUCTION: CHEMISTRY AND MATERIALS

All the solids around us, natural and man-made, are materials and the science of materials is the effort to understand the relationships between structure and properties so that structures can be selected and constructed to have the properties desired. The properties in question are nearly always physical: chemical reactions, on or within solids are the subject matter of chemistry proper, though perhaps an exception could be made in the case of ionic migration.

Chemistry has impacted on the science of materials in two ways. First, it has brought new methods to the synthesis of solids. Traditional methods of making ceramics, glasses, and so on were optimised largely by empirical means, some going back hundreds (if not thousands) of years: 'heat it and beat it' is a phrase encapsulating the older ceramics industry, for example. Close study of the reaction mechanisms involved in forming solid phases from precursors has made it possible to use much lower temperatures to make ceramics (the so-called 'chimie douce', or gentle chemistry route) which, with sol-gel processing, has revolutionised production of these materials. [1] Similarly, to deposit thin films (not just in the semiconductor industry but in anti-abrasion surface hardening and optical coating) decomposing organometallic molecules (Metal-Organic Vapour Phase Epitaxy) has proved a notable advance over the 'engineering' approach of flinging atoms at a cold surface in an ultra high vacuum.

The second way that chemistry has widened the perspectives of materials science will, in the long run, certainly prove more influential even than the control of synthesis. It lies at the core of the whole discipline of chemistry, and in enlarging the range of the possible by synthesising new lattices of atoms and molecules not previously found in the natural or manmade worlds. Such lattices are much more complex than hitherto, providing unit cells bordering on the mesoscopic, and give access to properties not previously observed. One aspect of this novelty is the concept of *self-assembly*.

LONG AND SHORT RANGE ORDER

We can classify solids by the degree of order in the structures through the concept of a *correlation*

---

function, defined by the average value of the product of two vectors, representing the position or orientation of the contents of a given unit cell and the other the corresponding arrangement at a given distance from the first [2]. If the positions and orientations of the contents of the remote region map completely on to that of the reference cell the average value of the vector product is unity, while if there is no correlation between them the correlation function is zero. We can define both short and long range correlation functions and classify solids by the length scale over which correlation exists. Thus *amorphous* solids show correlation between atom positions over short range but not long. Glasses (which may be formed by polyhedral SiO_4 and PO_4 sharing vertices, or even by random atomic distributions in metals) are isotropic on length scales much larger than interatomic. However, other classes of solid may be disordered in more complicated ways. *Liquid crystals*, for example, show long range structural correlation in one or two dimensions simultaneously with only short range correlation in the third. Solid polymers, too, having covalent backbones, show anisotropic atom-atom correlations which lead to unusual dynamical behaviour.

Infinite correlation lengths in three dimensions characterise the *crystalline state* where, the infinitely repeating units can be not only single atoms but also molecules. In a *continuous lattice* solid like SiO_2 or Al_2O_3 no molecular units can be distinguished, but a *molecular crystal* like CO_2 or naphthalene dissolves or vaporises into molecules rather than atoms. A particularly interesting class of crystals, which have become more and more important in recent years, combines the characteristics of continuous and molecular in the same lattice, for example continuous layers interleaved by molecular units, as in the layer perovskite salts $(C_nH_{2n+1}NH_3)_2MX_4$ [3]. A final category of solid is the *'composite'*, strictly speaking a two-phase material in which exceptional mechanical properties are conferred by small particles of one kind of material within the matrix of another on a mesoscopic scale, that is, in the range $10-100\,nm$. Thus we have metal-matrix or polymer-matrix composites, for instance incorporating carbon fibres (Table 1).

Table 1 Some solids showing single and composite chemical bonding

	Ionic	Covalent	Metallic	Van der Waals
Ionic	NaCl	K_3C_{60}	$K_2(CN)_4Br_{0.30}2H_2O$	TaS_2
Covalent		Si		C_{60}
Metallic			Cu	$(BEDT-TTF)_2X$
Van der Waals				Xe

SIMPLE AND COMPOSITE CHEMICAL BONDING

In real solids the classical paradigms of ionic, covalent, metallic and Van der Waals bonding are augmented by many other more interesting possibilities. Table 1 lists a number of cases where two distinct bonding modes coexist in the same crystal lattice. For instance in a crystal of C_{60} intramolecular C–C bonds are certainly covalent but the interaction between C_{60} is of Van der Waals type although at low temperature more specific interaction develops between C–C double bonds on one C_{60} and the C_5 rings on its neighbours (Fig. 1a). These differences are relevant to the dynamics of the C_{60} crystal: free rotation of the molecules at high temperature is replaced by finite jumps at the temperature is reduced, inducing a series of structural phase transitions [4].

When C_{60} forms superconducting K_3C_{60}, ionic interactions are added to the covalent and Van der Waals ones (Fig. 1b) [5]. More unusual are cases such as $K_2Pt(CN)_4Br_{0.30}2H_2O$ (commonly called KCP) where metallic bonding in one dimension is combined with ionic bonding in directions orthogonal to the chain of metal atoms [6]. Even more peculiar are the superconducting molecular charge transfer salts like $(BEDT-TTF)_2X$ where BEDT-TTF is bisethylenedithiotetrathiafulvalene, a quasi-planar organo-sulfur molecule, and X is an inorganic anion such as I_3^- $AuBr_2^-$, $Cu(NCS)_2^-$, etc. The metallic character arises from overlap of frontier molecular orbitals on neighbouring molecules which, however, are charged and so interact primarily by Coulomb forces with the polyatomic anions [7]. The crystal structure of one such compound is shown in Fig. 2.
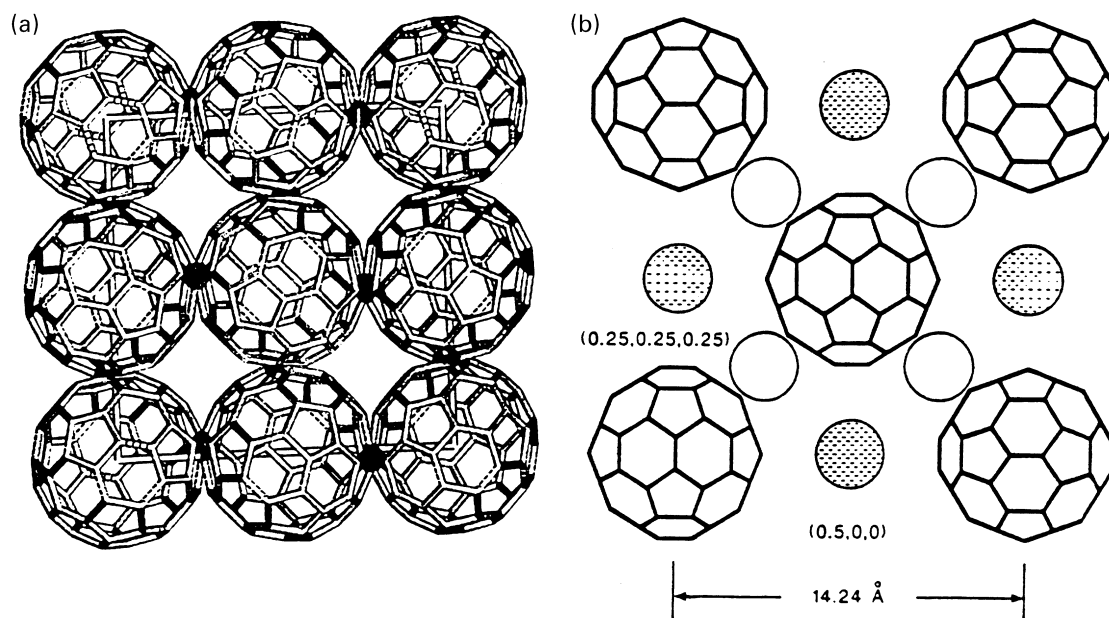
(a)

(b)

(0.25,0.25,0.25)

(0.5,0,0)

14.24 Å

Fig. 1 The crystal structure of (a) C_{60}, (b) K_3C_{60}.

PHYSICAL PROPERTIES AND THEIR COMBINATIONS

The physical properties of solids are rarely the sum of properties attributable to the individual components. For example, in a molecular superconductor the superconductivity of one molecule is a nonsense—the property is a *collective* one, belonging to the aggregate. One could make the analogy with extrinsic and intrinsic thermodynamic properties, e.g. temperature cannot be ascribed separately to each unit in a solid ensemble.
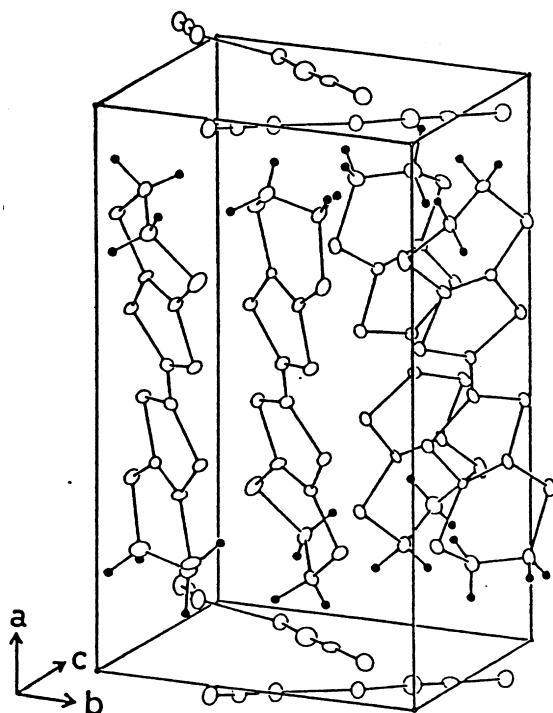
a

c

b

Fig. 2 The crystal structure of $(BEDT-TTF_2)Cu(NCS)_2$ [8].

The properties of interest to chemists are often the ones studied in simple prototypical solids many years ago by the physicists, though with the proviso that (because chemists make much more complex ensembles) new properties or combinations may arise that challenge the simple paradigms. Properties are divided into those which arise from the cohesive forces binding the crystal and those classed as 'electronic'. Among the former are thermal properties such as specific heat, and mechanical properties like compressibility. It might appear that hardness would also come into the same category, but in practice it is rarely an intrinsic property, being determined more by isolated and extended defects and dislocations. Chemists have not thought much about mechanical properties, certainly not with a view to designing such properties into the structure. However, matching the observed compressibility (and its pressure dependence) is a sensitive method of calibrating the interionic and intermolecular potentials used in the structure simulations [9].

Just as that many of the most interesting solids have more than one mode of chemical bonding in their lattices, so many interesting properties arise not alone but by combining physical phenomena. For example, thermally induced phase transformations combine with differences in optical behaviour in two phases to give the property of thermochromism. Stress, too, influences other physical properties, leading to the technologically important properties of ferroelectricity, ferroelasticity and magnetostriction. Likewise photon absorption gives rise to photochromism or photoconductivity, and even changes in magnetism, though photomagnetic effects are less well known. Finally electrical conductivity can be influenced by magnetic fields, most spectacularly in the so-called 'giant magnetoresistance' effects in $Ln_xSr_{1-x}MnO_3$[13].

The remainder of this survey exemplifies some of the points made above by considering two special topics. First I will describe some of the special features associated with the less well developed field of molecular materials. Second, to illustrate the diverse materials that can exhibit a single property, some examples are given from the field of superconductivity.

MOLECULAR SOLIDS: A NEW HORIZON FOR SOLID STATE CHEMISTRY

The paradigms of physical behaviour in the solid state are based on prototypes with simple crystal structures, containing only one to three atoms in the chemical unit cell. Such is the variety of electronic structure accessible by permuting of 90 stable elements in the periodic table, that all the bonding types are already available even in this limited subset. In respect of one physical property (electronic conductivity) the situation is encapsulated in Fig. 3. Conductivity is a property that spans the largest number of orders of magnitude of any in the universe: 28 from the most conducting metal to the most insulating solid substance. As seen from the left hand side of Fig. 3, the majority of the examples are in fact elements. On the right hand side, though, is another group of materials whose conductivities span just as wide a range as the simple ones, but whose formulae are more elaborate. They are all molecular solids. Among them are metals as conducting as copper, and also superconducting (which copper is not); semiconductors that can be doped in a similar way to silicon, and insulators as resistive as the purest ionic crystals. So, parallel to the more familiar solid state of continuous lattice materials, is the world of molecular solids.

Given that so many fascinating and useful properties arise from continuous lattice solids, you may ask why one should bother with these much more complex ones. Several convincing answers can be given. First, they are prepared in quite different ways from conventional metals and ceramics, at or close to room temperature, and usually from solution. Thus they give the solid state chemist access to the wider world inhabited by the coordination, organometallic and organic chemists. The implication is that contemporary synthetic virtuosity can be harnessed to the solid state.

A second obvious feature distinguishing molecular arrays is orientational order: either whole molecules or their side chains, can change their relative orientation as a function of temperature, pressure, stress, applied fields, etc., bringing about phase transitions that cause macroscopic changes in physical properties. One has only to think of liquid crystal displays to see the implications. Allied to orientation is the issue of anisotropy: low-dimensional conductivity [14], and deposition of oriented thin films (for example by Langmuir Blodgett dipping) are examples.
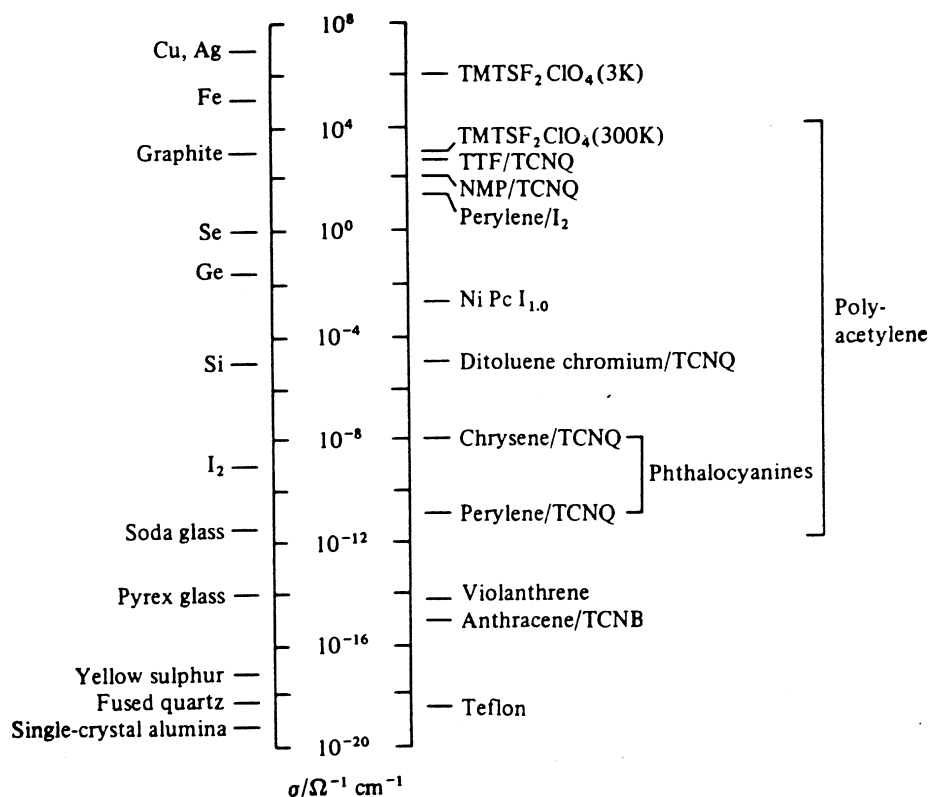
Fig. 3 Electrical conductivity of continuous and molecular solids.

SUPERCONDUCTIVITY: THE ROLE OF CHEMISTRY

From its discovery in 1910 up to the 1980s, superconductivity was not of much interest to chemists. The materials concerned were firmly in the realm of the metallurgist and the materials scientist, while the theory was couched in terms of wave vectors and phonons that made it accessible only to physicists. Even the theoretical prediction that one needed to maximise the electronic density of states at the Fermi surface and increase the electron-phonon coupling was scarcely a recipe for action by a synthetic chemist. Since then, of course, superconductivity has entered chemistry in a big way: an object lesson in materials chemistry.

We only need to look at the evolution of the critical temperature (T_c) with time (Fig. 4) to see how important it has been to the progress of the subject to examine new categories of material. Within each set of materials in Fig. 4, the first steps were the most significant so that, over time, further steps within the same material class gave rise to more modest progress. Thus exhausting the entire set of elements yields a maximum T_c of 9.2 K, while extending the field to binary phases took T_c up to 23 K (though it took 30 years to do so). The probability is that the line representing the mixed valency copper oxides is close to saturating, while with the discovery of the superconducting fulleride salts such as the one in Fig. 1b, the trend for molecular materials remains firmly upwards.

After the epoch making discovery by Bednorz & Müller [15] of superconductivity in a phase mixture containing La, Ba, Cu and O, whose composition they did not know, many solid state physicists converged on the problem with the result that many physical properties were measured on distinctly ill characterised samples. Only with preparative solid state chemistry methods could single phase samples of $La_{2-x}Ba_xCuO_{4-\delta}$ and $YBa_2Cu_3O_{7-\delta}$ be prepared, so that the structures and properties [17] could be studied in a definitive way. An example of the subtlety of these structures is shown in Fig. 5, which also illustrates how important it is to determine them in real space, by electron microscopy, and not only by diffraction.

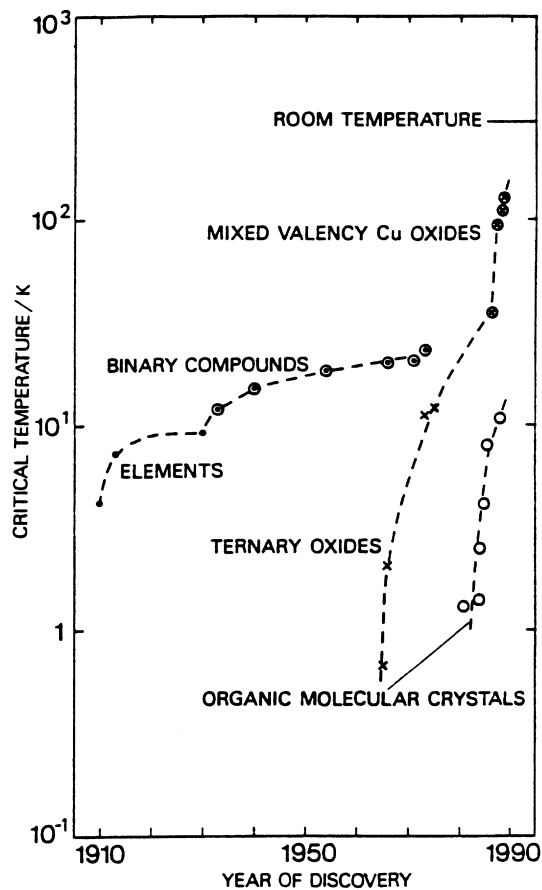In Fig. 5, the resolution is about 1.5 Å, so the black dots are images of individual columns of atoms,

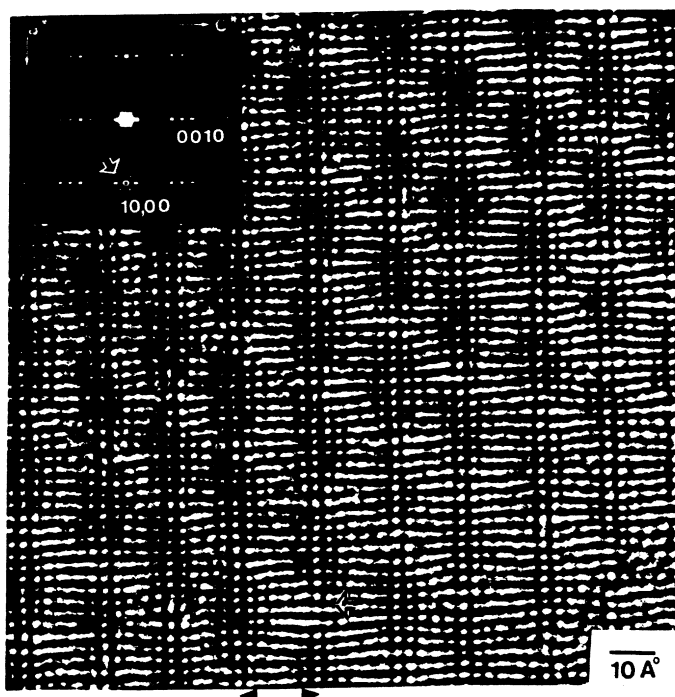**Fig. 4** Superconducting critical temperatures for various classes of material.

Fig. 5 Lattice image of $Bi_2Sr_{2+x}Ca_{1-x}Cu_2O_8$ observed by high resolution transmission electron microscopy [17].

projected parallel to the electron beam. The darker atoms are the ones with the largest atomic number, i.e. Bi, which form double layers. Two features stand out, showing how tricky it is to prepare and characterise such phases. First, along the Bi layers it becomes clear that the Bi–Bi distances are not equal but undergo a sinusoidal modulation.

This is an example of an incommensurate structure, so called because the periodicity of the modulation is not a rational multiple of the Bi–Bi separation. Second, it is also apparent that the separations between the Bi layers are not equal. Actually there are two different separations: 15 Å and 19 Å, the first corresponding to two CuO coordination polyhedra between BiO and the latter to three. Such an arrangement is called an *intergrowth* because what we are looking at is a mixture of two phases on an atomic scale. Inspection shows that the sequence, 15, 19, etc. is not alternating, but random. Consequently, to define a pure phase so that one could carry out definitive measurements of its physical properties would mean the most careful control of preparative conditions.

CONCLUSION

The foregoing example shows how closely chemistry has become woven into the science of materials. The other superconductors in Fig. 1 and 2 bear the same message. Similar examples could be given from other classes of physical property, especially from the burgeoning category of materials based on molecular building blocks. The conclusion is that 'materials chemistry' is now firmly of age.

REFERENCES

1   J. Rouxel, M. Tournoux, R. Brec. *Soft Chemistry Routes to New Materials*. Trans Tech Publications, Switzerland (1994).

2   M. E. Fisher. *Lectures in Theoretical Physics*, Vol. VII C, p. 61. University of Colorado Press, Boulder (1965).

3   P. Day. *Phil. Trans. Roy. Soc. A* **314**, 145–158 (1985).

4   W. I. F. David, R. M. Ibberson, J. C. Matthewman, K. Prassides, T. J. S. Dennis, J. P. Hare, H. W. Kroto, R. Taylor, D. R. M. Walton. *Nature* **353**, 147–149 (1991).

5   P. W. Stephens, L. Mihaly, P. L. Lee, R. L. Whetten, S.-M. Huang, R. Kauer, F. Diederich, K. Holczer. *Nature* **351**, 632–634 (1991).

6   J. M. Williams, A. J. Schultz. In *Molecular Metals* (W. E. Hatfield, ed.), pp. 337–368. Plenum Press, New York (1979).

7   P. Day. In *Encyclopedia of Advanced Materials* (D. Bloor, R. J. Brook, M. C. Flemings and S. Mahajan, eds), pp. 417–421. Pergamon Press, Oxford (1994).

8   H. Urayama, H. Yamochi, G. Saito, S. Sato, A. Kawaryoto, J. Tanaka, T. Mori, Y. Maruyama, H. Inokuchi. *Chem. Lett.* 463–466 (1988).

9   C. R. A. Catlow. In *New Trends in Materials Chemistry* (C. R. A. Catlow, A. K. Cheetham, eds), pp. 141–194. Kluwer Academic Publishers, Dordrecht (1997).

10   C. Kittel. *Introduction to Solid State Physics*. John Wiley, New York (1976).

11   A. K. Cheetham, P. Day, eds. *Solid State Chemistry: Techniques*. Clarendon Press, Oxford (1987).

12   P. N. Prasad. In *Lower Dimensional Systems and Molecular Electronics* (R. M. Metzger, P. Day, G. Papavassiliou, eds), pp. 563–572. Plenum Press, New York (1990).

13   A. Maignan, V. Caignaert, Ch. Simon, M. Hervieu, B. Raveau. *J. Mat. Chem.* **5**, 1089–1091 (1995).

14   P. Day. *Chem. In Br.* **19**, 306–314 (1983).

15   J. G. Bednorz, K. A. Müller. *Z. Phys. B* **64**, 189–193 (1986).

16   e.g. W. I. F. David, W. T. A. Harrison, J. M. F. Gunn, O. Moze, A. K. Soper, P. Day, J. D. Jorgensen, D. G. Hinks, M. A. Beno, L. Soderholm, D. W. Capone, I. I. I. K. Schuller, C. U. Segre, K. Zhang, J. D. Grace. *Nature* **327**, 310–312 (1987).

17   P. L. Gai, P. Day. *Physica C* **152**, 154–156 (1988).