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Neutron Powder Diffraction and High T_c Superconductors

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Neutron powder diffraction is a technique for determining the crystalline structure and texture of materials for which single crystals cannot be obtained. As such it has made important contributions to the characterisation and understanding of the new high temperature superconductors. As well, NPD has wide applications in materials science, ranging from the study of catalyst and zeolite structures, to the texture of railway lines and composite superconducting wires.

The arrangement of atoms in a material ('crystal structure') largely determines its properties. Crystal structure determination is then one of the basic requirements for any new substance, whether it be a pharmaceutical drug or an electronic material. Classical methods of structure determination involve the growth of single crystals, their orientation by a computer-controlled diffractometer, and the measurement of the intensity of X-rays reflected from all possible atomic planes. Powerful methods then exist for performing the Fourier transform of this diffraction pattern to obtain the real-space structure. However, many interesting materials do not form single crystals. The crystallites of such materials are microscopic or 'powdered', and powder diffraction is needed for their study.

Powder diffraction means that reflections from all possible atomic planes are obtained simultaneously, without orientation of the material. Sorting out which intensities belong to which planes has only been possible with the advent of computer methods of 'profile refinement', invented in Petten (the Netherlands) by H.M. Rietveld in 1967. Rietveld refinement was developed for the study of magnetic structures using neutron diffraction, and at first was used only by a few specialists. Today it is the standard technique for all powder diffraction structural work, with X-rays as well as with neutrons.

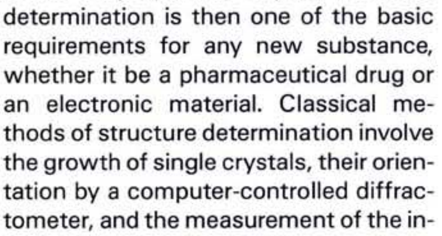

Fig. 1 — Schematic diagram of the very high resolution neutron powder diffractometer D2B at ILL.

Powder diffraction is particularly useful for the study of materials which undergo structural transitions at low temperature, since single crystals of such materials, even if they can be grown, usually break up or become multi-domain when the crystal symmetry is lowered with the transition. For example, the new heavy metal copper oxide superconductors $(La,Sr)_2CuO_4$ and $YBa_2Cu_3O_7$ undergo such transitions, making it difficult to obtain single crystals. In normal superconductors, soft-phonon vibrational modes associated with structural transitions can contribute to the electron-phonon coupling of electron pairs at the heart of the classical BCS mechanism, so the study of structural transitions is of interest in itself.

Neutron powder diffraction is especially useful for such problems. Oxygen co-ordination is one of the most vital questions for inorganic materials, determining for example the valence state of metals, and hydrogen co-ordination is similarly important for organic structures. But hydrogen and oxygen have few electrons to scatter X-rays, and are not easily seen in the presence of heavy elements. Neutrons though, are scattered just as strongly by these light atoms as by heavy metals. The vital structural question for the new copper oxide superconductors has been the oxygen co-ordination and the valence state of copper.

Neutrons have a magnetic moment, and are strongly scattered by the magnetic moments of unpaired electrons on magnetic atoms. According to Anderson's resonating-valence-bond theory, magnetic coupling of electron pairs is

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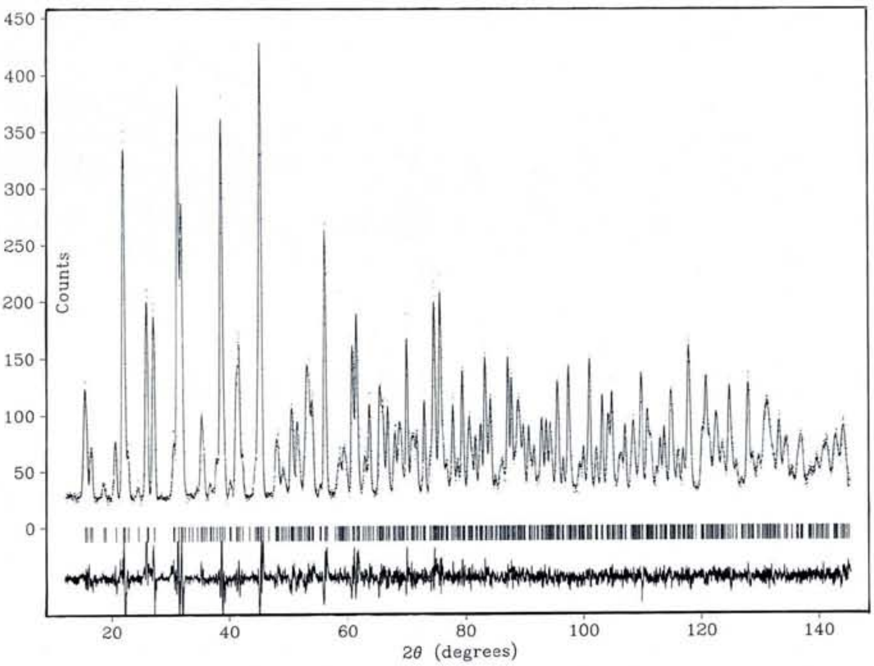


Fig. 2 — Observed and calculated neutron diffraction 'profiles' for a Geneva sample of superconducting $YBa_2Cu_3O_7$ made at 5K with a 1.04996 Å beam.

the basis of superconductivity in the new materials. Neutron diffraction has then been essential in demonstrating magnetic interactions in the copper oxide superconductors, though magnetism appears in a slightly different oxidation state, and may simply be a competitor to superconductivity.

The new superconductors are then ideal examples of the application of neutron powder diffraction: single crystals cannot be easily obtained, structural transitions break up such crystals, light atoms must be located in the presence of heavy metals, and magnetic ordering may be important.

Neutron Powder Diffraction Methods

The neutron powder diffractometer is conceptually very simple (Fig. 1). A monochromator crystal focusses a discrete wavelength neutron beam λ onto a powder sample of several cm^3, usually in a cryostat or furnace. Sample environment is simplified because neutrons are very penetrating. Each crystal plane scatters neutrons by an angle Θ, determined by the d-spacing of the plane, according to Braggs law $\lambda = 2d\sin\Theta$, with the intensity depending on the detailed atomic arrangement in the crystal. A large multidetector collects many of these Bragg reflections simultaneously. High resolution geometry is needed to separate the different reflections, but complete separation is not possible, especially for complex structures.

Rietveld refinement consists simply of refining the atomic co-ordinates and other parameters so that the calculated diffraction profile fits that observed (Fig. 2). Starting models are obtained either from preliminary X-ray work to locate the heavy atoms, or by 'direct methods' applied to a set of Bragg intensities extracted by peak stripping. Even if only some of the atoms are located, the remainder can usually be obtained by difference Fourier reconstruction based on the results of partial refinement. Known co-ordination and bond lengths are useful in selecting chemically reasonable starting models. Simple though the principle may be, a great deal of insight is needed to choose an optimum starting point and powerful computing facilities are required to perform the refinement processing.

Copper Oxide Layer Superconductors

Bednorz and Müller chose to look at perovskite ABO_3 oxides where the B metal atom, *e.g.* Ni or Cu, can have different valence states. The idea was, following BCS ideas of electron-phonon interaction, to try to couple instabilities in the perovskite structure, well known to be responsible for ferroelectric structural transitions in materials such as $BaTiO_3$, to electron transfer due to possible valence fluctuations. The Jahn-Teller distortion of the CuO_6 perovskite octahedron, expected for Cu^{++} but not for Cu^{+++}, might produce such coupling. Materials developed earlier in France by Raveau, by doping La_2CuO_4 with Sr to produce Cu^{+++}, were shown after many trials to be indeed superconductors, with surprisingly high T_c.

An even better example, $YBa_2Cu_3O_7$, was found by Chu and others by trial and error, and more recently, other copper oxide superconductors have been discovered with Bi-oxide layers (also suggested by Raveau's group). Even higher T_c has been obtained by replacing Bi by Pb (partially) or Tl (wholly), but the essential copper oxide layers in these materials appear to be very similar to that in the original Bednorz and Müller compound when characterised by X-ray and neutron diffraction.

Neutron powder diffraction was first used at Argonne to show that La_2CuO_4 does indeed have a structural transition, which moves to low temperature with Sr-doping, but that it involves tilting of the CuO_6 octahedra (Fig. 3), not strongly coupled to the copper valence state, rather than a Jahn-Teller distortion of the Cu-O bonds. Transitions involving tilted octahedra are very common among perovskites (*e.g.* $SrTiO_3$). The most important features are the puckered copper oxide planes, where the Cu has four close O within the plane, plus two more distant O at the apexes of the elongated octahedron. The average valence of Cu is indicated by the distance of these out-of-plane O, which are also mainly involv-

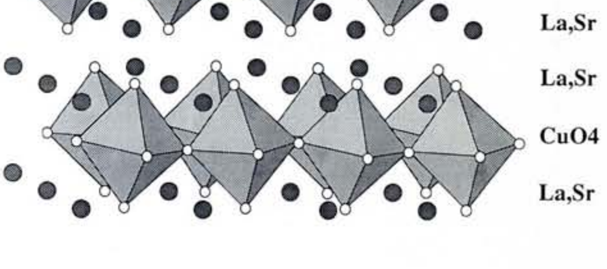


Fig. 3 — The original $(La,Sr)_2CuO_4$ superconductor discovered by Bednorz and Müller. The Cu atoms (not shown) are at the centre of the octahedra formed by the O atoms.

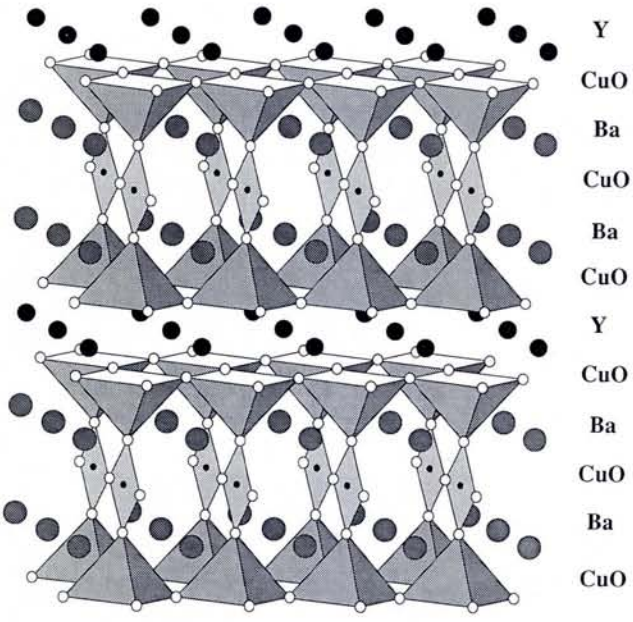


Fig. 4 — The structure of superconducting $YBa_2Cu_3O_7$.

ed in the tilting transition. Such details of oxygen co-ordination are best obtained by neutron diffraction.

Neutron powder diffraction was most spectacularly successful in determining the structure of the second high T_c superconductor, $YBa_2Cu_3O_7$. X-ray single crystal diffraction had already found the heavy atoms, but had concluded in a disordered oxygen defect structure, and this was thought to be important for the exceptionally high T_c (95 K). Moreover, at least two quite different oxygen co-ordinations for Cu (both wrong) were proposed on the basis of chemical arguments and X-ray results. Neutron powder experiments at several different laboratories on both reactors (*e.g.* Grenoble) and accelerators (*e.g.* Argonne and RAL) agreed that instead the structure was well ordered, and contained unique 1D CuO chains connecting the usual copper oxide planes (Fig. 4).

The reason the X-ray work was inconclusive was that the material was not a true single crystal, but microscopically twinned, and because X-rays cannot locate the light oxygen atoms very precisely in the presence of the heavy metals. It should be noted that until the exact oxygen content was known, it was not even possible to write down the chemical formula. The effective valence of copper (on average 2.3) could again be obtained from the precise Cu-O bond lengths obtained by neutron diffraction; it was found that Cu^{+++} was distributed over the two different copper sites, in the plane and in the chain.

A fascinating feature of $YBa_2Cu_3O_7$ is that oxygen in the chains can be driven off above 750 K, and the material then becomes a normal Cu$^+$/Cu^{++} semiconducting copper oxide $YBa_2Cu_3O_6$ (Fig. 5). This oxygen can be replaced at lower temperatures. The details of this oxidation-reduction has been studied by *in-situ* neutron powder diffraction, which shows how the valence of copper in the two sites changes on going from the superconductor to the semiconductor. This kind of information is helpful not only for basic science, but also for the practical fabrication of the material.

The CuO chains in $YBa_2Cu_3O_7$ were clearly so important that much effort was expended in investigating the structure of similar materials which were *not* superconductors, in particular with some interesting neutron powder experiments at RAL Oxford and NBS Washington. More recently, Geneva-Grenoble work showed that the chains may be involved in a structural transition in which they zig-zag slightly, with the chain oxygen occupying one of two potential minima just off the chain axis. The resulting anharmonic oscillations might explain why, if phonons are after all important for superconductivity, the isotope effect is small for this material.

One important structural result which must be attributed to electron rather than neutron diffraction, was the finding in Grenoble that there is a superstructure involving missing chains for oxygen deficient material $YBa_2Cu_3O_{7-x}$, for a large range of x near 0.5; T_c for this phase drops sharply to 60 K.

For $x > 0.6$, $YBa_2Cu_3O_{7-x}$ becomes a semiconductor with magnetic ordering at low temperature. The magnetic structure was again obtained by neutron powder diffraction (at Brookhaven), but since this phase does not show the orthorhombic distortion, single crystals can be grown and have been used for more extensive studies both at Brookhaven and Grenoble. Magnetism can also be induced in $YBa_2Cu_3O_7$ by replacing the Y by a magnetic ion such as Gd, with little change to the superconducting properties. Interestingly, although the layers of Gd are separated by nearly 12 Å, Oak Ridge-Grenoble neutron powder work has shown that 3-dimensional magnetic order is established below 2.22 K, coupling across the CuO layers.

So superconductivity is lost with the disappearance of the chains, and competing magnetism takes over with the planar copper becoming almost entirely Cu^{++}. Until recently it seemed that the chains were essential for high T_c. It turns out though that they are 'merely' the filling between the CuO planes, the only common features in the new Bi- and Tl-oxide materials which have even higher T_c! Their importance is apparently to 'tune' the valence of the in-plane Cu

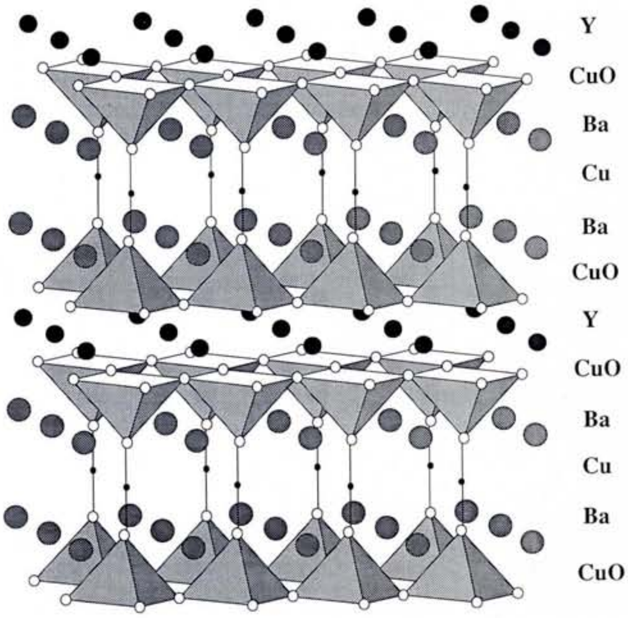
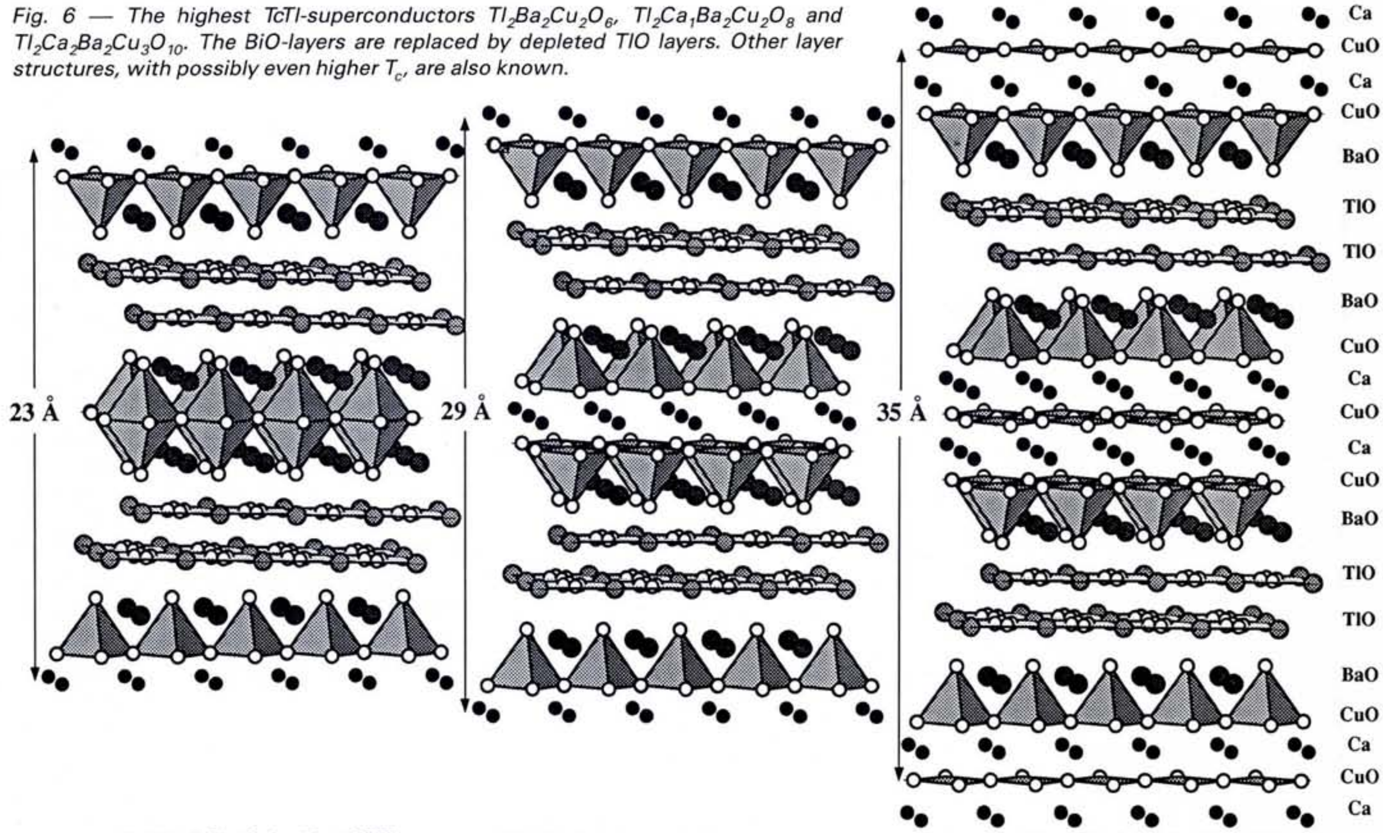


Fig. 5 — The structure of semiconducting $YBa_2Cu_3O_6$.

Fig. 6 — The highest TcTl-superconductors $Tl_2Ba_2Cu_2O_6$, $Tl_2Ca_1Ba_2Cu_2O_8$ and $Tl_2Ca_2Ba_2Cu_3O_{10}$. The BiO-layers are replaced by depleted TlO layers. Other layer structures, with possibly even higher T_c, are also known.



Tl2Ba2CuO6 Tc=80K **Tl2Ca1Ba2Cu2O8 Tc=105K** **Tl2Ca2Ba2Cu3O10 Tc=125K**

via its distance to the out-of-plane O, and in the new materials this rôle is taken over by the BiO or TlO layers.

Neutron powder diffraction has already been used in Grenoble to refine the structure of these new materials. For the $T_c = 80$ K phase it was possible to decide between conflicting X-ray models for the BiO layers, to determine the oxygen co-ordination and hence the valence of Cu (again 2.3 on average), and to show that the superstructure is due to BiO in-plane displacements. The oxygen in the center of the B-square is too far away for Bi^{+++}, and therefore moves toward the Bi-atoms, reducing the subcell symmetry, probably to A2aa.

The various phases of the Tl-superconductors have also been examined by neutron powder diffraction $Tl_2Ca_1Ba_2Cu_2O_8$ (2122) and $Tl_2Ca_2Ba_2Cu_3O_{10}$ (2223) by Dupont-Brookhaven and ILL-Oak Ridge, and $Tl_2Ba_2Cu_1O_6$ (2021) by ILL-CNRS. The structures (Fig. 6) are similar to those for the Bi-materials, with oxygen displaced from the centre of the Tl-squares to satisfy the 3+ valence of Tl. The superstructure is much less obvious, but electron diffraction indicates a charge density wave in the TlO layers, at least in the 2122-phase. Depending on the heat treatment, the TlO layers can be depleted, and the 2021-phase then becomes tetragonal and superconducting, whereas samples with nearly complete TlO layers are orthorhombic and non-conducting. However, the structural requirements, for superconductivity in the Bi- and Tl-materials are as yet less well understood than in $Y_1Ba_2Cu_3O_7$.

Other Applications of Neutron Powder Diffraction

Neutron powder diffraction was of course well established before the appearance of high T_c superconductors! The same kind of problems exist for many different real materials, ranging from solid liquids and gases, to ionic conductors and hydrides used for hydrogen storage. Even the crystal chemistry of the common lead-acid battery is not yet understood because of obvious difficulties with conventional single crystal X-ray techniques of locating oxygen and hydrogen in the presence of the heavy metal. One of the most interesting applications is to the location of molecules absorbed by zeolite catalysts.

All synthetic zeolites, which are used extensively as catalysts in the petrochemical industry, are produced as powders or microscopic crystallites. The catalytic properties apparently depend on the location of absorbed hydrocarbons and the identification of chemically active sites. Reactor-based neutron diffractometers are well suited to such large structures because of the long wavelength neutrons available. Typifying such applications, a combination of neutron powder diffraction and neutron small angle scattering, has been used in Grenoble to locate clusters of a simple hydrocarbon (benzene) in Y-zeolite. By constraining the molecule and the zeolite framework to their known geometry, the number of parameters can be greatly reduced in special profile refinement procedures.

Finally, neutron powder diffraction can be used to study the texture of materials, as well as their crystal structure. For example, Karlsruhe-Grenoble work has shown how strains develop in bundles of superconducting wires due to a phase transition, limiting current carrying capacity. Actual cm-diameter wire bundles, together with the prestressed steel and copper matrix, are transparent to the neutron beam because of its low absorption compared to X-rays.

Similar methods are used to measure interior strain in welds in oil pipes at Chalk River in Canada, and the work hardening of European railway lines in Grenoble. Such experiments may seem prosaic compared with the exciting structural work on the new superconductors, but they are nevertheless extremely important economically.

General Reference and Bibliography

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