

C1.7.2 Neutron Techniques: Crystallography

Why use Neutrons ?

Ceramic superconductors are generally heavy metal oxides, and neutron diffraction has long been superior for the precise location of light atoms, such as hydrogen and oxygen, in the presence of heavy atoms. While X-ray scattering is proportional to atomic number (X-rays are scattered by electrons), neutron scattering is a nuclear reaction, so the scattering power may be as large for oxygen as it is for lead. This is important if we are to understand the oxidation state of these materials, which controls their superconducting temperature. In practice, neutron diffraction is no more difficult to perform than X-ray diffraction, except of course that it must be done in a central laboratory rather than in the local basement.

A second reason for using neutron diffraction is that new materials are often only available in polycrystalline or 'powder' form. While X-ray studies (C1.1) and electron diffraction (C1.2) may be superior for initial structure determination, neutron powder diffraction provides a more precise measure of structural details. For example, precise measurements of metal-oxygen distances with neutron diffraction can be used to determine the valence state of the metal ions. It was this kind of measurement that resulted in the idea that superconductivity in layered copper oxides can be controlled by the oxidation/reduction of "charge reservoir" layers, a concept that led to the successful search for new materials with thallium, bismuth or mercury oxide charge reservoirs.

Neutron diffraction is also important because neutrons are scattered by magnetic moments, and magnetic coupling of electrons is believed to be necessary for high-T_c superconductivity. Neutrons as well have energies comparable to the atomic and magnetic excitations in crystals, so are unique for measuring crystal dynamics; electron-phonon coupling is the basis of classical superconductivity theory. Finally, longer wavelength neutrons can be used to obtain small angle scattering pictures of the magnetic flux-line lattice (C1.7.3).

The Neutron Advantage for Structure Refinement

The advantage of neutron diffraction for locating oxygen is obvious from figure 1, which compares the scattering powers of the different atomic constituents of high temperature superconductors for electrons, X-rays and neutrons. X-ray scattering is proportional to the number of electrons, and electron scattering depends on the electrical potential, which also depends on the atomic number. However, neutron scattering, which depends on the properties of the nuclei, is of similar magnitude for all of these atoms.

Furthermore, the scattering centres for X-rays and electrons are not nuclear points, but are instead atomic spheres of finite dimension d . The scattering power for X-rays of wavelength λ then falls off rapidly with scattering angle 2θ , decreasing by half when $\sin\theta = \lambda/d = 1$, since $\lambda \approx d$ (the X-ray wavelength is comparable to the size of the atoms). Thermal neutrons, with similar wavelength, are scattered by the much smaller nucleus, so $\sin\theta$ can have large values without any fall-off in intensity. Large values of $\sin\theta$ are needed to obtain high resolution of structural details.

Finally, neutrons are much more penetrating than even X-rays, so can easily be used with complex sample environments (temperature, pressure). And of course, neutrons are uniquely sensitive to magnetism, intimately connected with superconductivity.

Neutrons would in fact be ideal but for two disadvantages. Firstly, the experimenter must travel to a central neutron source, usually a nuclear reactor, to perform the experiment; a physicist might find this normal, but a chemist usually has all the equipment he needs in his own laboratory. Secondly, even the best reactors produce far fewer neutrons than the number of photons produced by an ordinary X-ray tube. Low intensity is compensated to some extent by the higher penetrating power of the neutron, which permits much larger samples; large samples are actually an advantage, since better averages for polycrystalline materials are obtained, with fewer systematic errors.

Neutrons have another disadvantage when nothing is known about the structure. With X-rays it is only necessary to locate the heavy atoms, and the remainder can then be obtained by difference techniques. Neutron diffraction is then almost always a refinement technique, but then most of the physical and chemical interest is in these details.

Neutron Diffraction and the Characterization of Superconductors

One of the key questions about new materials concerns their precise atomic structure and stoichiometry. For example, figure 2 compares the structure of the original 90K superconductor, $\text{YBa}_2\text{Cu}_3\text{O}_7$ as obtained with X-rays at Bell laboratories [1], and as obtained with neutrons at ILL Grenoble [2]; these are typical of the results obtained by several laboratories using the two techniques. Even though both the X-ray and neutron models are correct in principle, the X-ray model looks very different, and would be very misleading for chemists trying to make similar materials. It emphasizes the heavy atoms and appears to show that the material is simply an oxygen deficient perovskite, a common structure.

The neutron model emphasizes instead the oxygens, and shows that there are two very different kinds of copper, the one in the "chains" with 4-fold square oxygen co-ordination typical of Cu^{2+} and the other in the "planes" with 5-fold co-ordination indicating perhaps a higher copper oxidation state. Neutron diffraction also shows where the oxygen is lost when the material is reduced, destroying superconductivity. The oxygen atoms were simply not well located with the first X-ray experiments, and this gave a very different idea of the structure.

In particular, the neutron picture (figure 2b) shows that there are no CuO_6 octahedrae as drawn in the X-ray picture (figure 2a); there are just CuO_4 squares and CuO_5 pyramids. Since CuO_6 octahedrae were at the heart of Bednorz and Müller's idea [3] for oxide superconductors, the neutron results were at first contested, but are now universally accepted.

The unique results obtained with neutron diffraction have been one of the main influences in the understanding of the atomic structure of new high temperature superconductors. As we shall see, neutrons have also revealed something of the mechanism controlling the chemistry of these materials, which has helped chemists search for new superconductors with even higher T_c .

Neutron Powder Diffraction

Neutrons have a particular advantage when used with polycrystalline or 'powdered' material; because of the great penetrating power of the neutron, an average is obtained over many more crystalline grains than is possible with X-rays or electrons.

Powder diffraction, like classical crystallography, requires the measurement of the scattering power of the various crystal planes, but of course, with a powder it is not possible to select these planes by orienting the crystal, as it is with single crystals. The different planes are separated only by the different d-spacings between them, not by their orientation. Different d-spacings produce constructive scattering at different angles ($\sin\theta/\lambda$), and the neutron diffractometer must have high angular resolution to resolve the various "Bragg peaks". High resolution can be obtained by using a high monochromator "take-off" angle, with fine Söller collimators in front of the monochromator and detectors - a stack of thin neutron absorbing blades to define the direction of the neutrons to within a few minutes of arc [4].

The neutron beam from the reactor (figure 3.) is then defined by a Söller collimator, and a particular wavelength λ selected by the monochromating crystal. This monochromatic neutron beam is scattered by the powdered sample, and the intensity from the different crystal planes is measured by scanning a second Söller collimator in front of a detector through all scattering angles.

In practice, a multi-detector with a bank of collimators is used to speed up data collection. The germanium monochromator crystal is mechanically "squashed" or otherwise deformed to break it into small crystallites with a certain angular "mosaic spread", so that a band of wavelengths $\Delta\lambda$ is passed, again to increase the intensity. As well, the monochromator consists of up to 30 individual pieces aligned to vertically focus the neutron beam onto the sample. The various wavelengths are also focused in the horizontal plane so that they all pass through the parallel blades of the detector collimator after being scattered by the sample. 2°

For lower resolution work, a true position sensitive detector (PSD) can be used to speed up data collection. With a PSD, complete patterns can be obtained in a few seconds, which means that chemical reactions such as oxidation/reduction can be studied in real time. Here again the greater penetrating power of the neutron, and the larger sample volume, makes this easy compared to X-ray methods.

Rietveld Refinement and High-Tc Superconductors

The conflicting requirements of neutron powder diffraction are to use as many neutrons as possible, but to retain high angular resolution in the 'diffraction pattern' (figure 4.). Clearly there are many peaks, corresponding to different crystalline planes, which are still not resolved. One early solution was to use a peak stripping computer program to extract as many individual peaks as possible.

A major advance came when Rietveld [5] showed that rather than extract the individual peaks and use them to obtain the crystal structure, it is much better to refine the crystal structure to fit the observed diffraction "profile" directly. This is because the peak positions (d-spacings) are all determined by at most 6 parameters, the dimensions and angles of the primitive structure unit (unit cell). The peak intensities are all determined by the positions of the individual atoms in the unit cell for a periodic structure.

Rietveld refinement means that only physically real parameters, describing the structure, are refined, eliminating correlations between peak heights, positions etc that are inherent in a peak stripping procedure. The atomic co-ordinates obtained with neutron powder diffraction are often more reliable than those obtained with classical single crystal methods, because in practice it is very difficult to obtain good single crystals, and even when it is possible, the crystals may break up on undergoing structural transitions at lower temperature [6].

The powder experiment is also much easier and faster, and because of this the structure can be determined at many different temperatures, instead of the one or two temperatures usual with classical crystallography.

The inspiration for Bednorz and Müller's discovery of high temperature superconductors came in fact from their earlier work on perovskite ferro-electrics. They argued that small displacements of oxygen atoms, surrounding a 'mixed valence' cation such as copper, could provide the electron-phonon coupling thought to be necessary for superconductivity.

Figure 5 shows that the oxygen octahedra surrounding Cu^{2+} are normally elongated due to the so-called 'Jahn-Teller' distortion. No Jahn-Teller effect is expected for Cu^{3+} , so that if Cu^{2+} should lose an electron, the 'apical' oxygens should move in to form a more regular octahedron. Charge fluctuations on copper should then be strongly coupled to longitudinal vibrations (or phonons) involving the apical oxygens. Bednorz and Müller were of course spectacularly successful when, guided by this idea, they found that the perovskite $(\text{La,Sr})_2\text{CuO}_4$ was superconducting up to 35K, much higher than had previously been thought possible.

However, Rietveld refinement of neutron powder diffraction by Jorgensen et al. [8] immediately ruled out apical oxygen displacements toward copper, as imagined by Bednorz and Müller. Instead, they found a structural transition with *transverse* displacement of the apical oxygen associated with tilting of the CuO_6 octahedra (fig.6), of a type also common in perovskites, but not strongly coupled to the electronic charge. Neutron powder diffraction was then important for the understanding of oxide superconductors from the very beginning.

Charge Reservoirs and high T_c

Evidence for coupling between the charge on copper and the distance to the apical oxygen had to await detailed measurements on the second high temperature superconductor, the 90K material $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (fig.7). This material can be made non-superconducting simply by heating it to reduce the O4 oxygen content i.e. the oxygen in the charge reservoir CuO-chains. An obvious experiment was to use neutron powder diffraction to measure the oxygen content of these chains, and in particular the changes in the copper-oxygen distances, on passing from the superconducting to non-superconducting material.

Cava et al. [9] found that for well ordered samples, T_c varied with x as shown in figure 8a. Starting at 90K for $x=0$, T_c dropped first to a 60K plateau before falling to zero for $x > 0.6$. Remarkably, the Cu2-O1 distance to the apical oxygen showed similar changes (fig.8b) in contrast to the almost constant behaviour of the other copper-oxygen distances. Since the Cu2-O1 distance enters into the bond sum used to calculate the apparent valence of Cu2 in the conducting plane, it was concluded that the observed changes in T_c were directly related to the effective valence of this copper. The plateau at 60K was assumed to correspond to an intermediate superconducting phase, with about every second oxygen missing from the CuO-chains (the details of the structure of this second phase were later discovered).

Since the valence of copper in the conducting planes, and hence T_c , could be controlled by the structure and oxidation state of the charge reservoir, these neutron diffraction experiments lead to an intense search for new materials in which the CuO reservoir was replaced by other oxides. A great many different superconducting oxides were so discovered, and remarkably, materials with lead, bismuth and mercury oxide reservoirs were found to result in even higher T_c 's.

Single Crystal Neutron Diffraction

After new materials are discovered, and characterised with the help of powder diffraction, it usually becomes possible to grow single crystals, and this gives opportunities for further work with neutrons. Single crystal elastic scattering can be used to obtain structural details that may be missed with powder diffraction, since single crystals allow an exploration of 3D scattering space, while powder diffraction reduces to one dimension – intensity versus d-spacing. Single crystal inelastic neutron scattering can be used to investigate the dynamics of the structure, and also the magnetic properties of the atoms.

For example, single crystal diffraction has been used to examine the details of the intermediate phases of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ for $0 < x < 1$; for $x \sim 0.5$ for example, there is a distinct phase, with a different T_c , where every second oxygen is missing from the chains [10]. Single crystal neutron diffraction has also been used to find where a very small amount of extra oxygen goes in $\text{La}_2\text{CuO}_{4.032}$ and to investigate subtle phase separation in this material [11]. This extra oxygen, and its co-ordination to metal atoms, can have important effects on the superconducting properties.

Inelastic neutron diffraction has been important for investigating the dynamical properties of these materials, and especially the role of magnetic moments on the copper atoms [12]. Superconductivity is intimately connected with magnetism, and in copper oxide materials it is thought that electron coupling via magnetic interactions may in fact be responsible for superconductivity. Since neutrons themselves carry a magnetic moment, they are a unique radiation for investigating these theoretical ideas.

Conclusions

Neutron diffraction is a unique tool for structural inorganic chemistry where light atoms must be located in the presence of heavy atoms. Neutron powder diffraction is especially useful where structural transitions break up single crystals, or when single crystals are simply not available, which is often the case for new materials. The Rietveld refinement method is commonly used to fit the structure directly to the powder diffraction pattern, without the need to extract Bragg peak intensities. The precise measurement of metal-oxygen distances in oxide superconductors has helped in the understanding of the crystal chemistry, and in the search for new materials. But the study of superconductor chemistry is only one of many applications of neutron powder diffraction; others include the determination of magnetic structures and the physics of colossal magneto-resistive materials, ferro-electrics and structural phase transitions, in-situ electro-chemistry, the structure of zeolite catalysts etc. A more complete review of these different applications is given elsewhere [13].

References

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Figure Captions

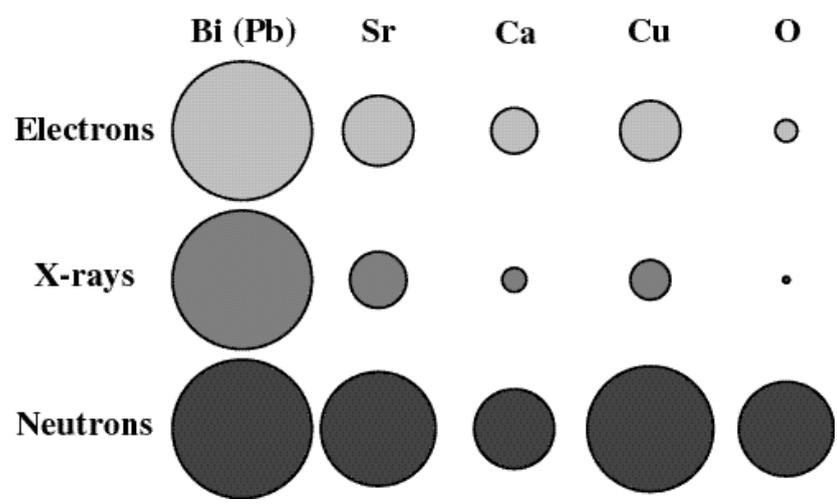


Fig.1. Relative scattering powers of the different atoms contained in high temperature superconductors, for electrons, X-rays and neutrons for scattering at $\sin\theta/\lambda=1$. Neutrons see the light oxygen atoms as easily as they see the heavy metal atoms.

