ABSTRACT: Neutron powder diffraction, with both reactor and pulsed neutron sources, has been important for our understanding of the structures of the oxide superconductors. These structures appeared very different when seen with neutrons, which emphasized the oxygen lattice, compared with X-rays, which emphasized the heavy metal atoms. Neutron diffraction first demonstrated the two dimensional nature of the early materials, and this lead to the successful search for new 2D superconductors based on the well known ‘Aurivillius’ structure. Neutron powder diffraction also played an important rôle in the developement of ‘charge transfer’ ideas of the electronic doping mechanism in oxide superconductors. Although it is not known if these ideas are relevant to the superconducting mechanism itself, they have guided chemists in the discovery of new materials. They have also helped us understand why oxidation sometimes increases Tc, and sometimes kills superconductivity, and how the distribution of electron holes between the different layers of a superconductor can be changed by effects such as pressure, which often produce unexpectedly large changes in Tc.

1. Introduction

1.1. NEUTRON POWDER DIFFRACTION AND HIGH TEMPERATURE SUPERCONDUCTORS

For a few days in March, all of the world’s major laboratories struggled to understand the structure of the 90K superconductor, using every possible technique. The results at the end of the month can be summarised by figure 1. It shows a typical X-ray picture of the structure of the superconductor [1], beside a typical neutron picture of the ‘same’ structure [2].

The X-ray and neutron pictures in figure 1 are both technically correct. They both show defect perovskite structures, with some oxygen missing, and they agree about where this oxygen is missing, and about the positions of all of the cations. In fact, the X-ray structure was used as a starting point for the neutron refinement. Yet the neutron work gives an entirely different picture of the structure. The X-ray drawing shows CuO₆ octahedrae, as believed necessary for high Tc according to Bednorz and Müller’s ideas [3]. The neutron picture shows no such octahedrae, but instead 2-dimensional planes of copper oxide pyramids, connected by 1-dimensional chains of copper oxide. The absence of octahedrae was at first strongly contested [4], and this controversy helped to make the neutron paper [1] the most cited experimental work in the field during the following year [5]. The one- and two-dimensional nature of the 90K superconductor excited the interest of theoreticians, and stimulated chemists to look for superconductivity in other 1- and 2-D perovskite materials.
Fig. 1. Structures of the 90K superconductor
(a) ‘Ba₂YCup₂O₆’ obtained by X-rays [2] and of
(b) ‘Ba₂YCup₂O₉’ obtained by neutrons [1].

The differences between the two drawings were due simply to the fact that X-rays could not locate all of the light oxygen atoms, especially in a polycrystalline material. This story would later be repeated, when another famous laboratory, again using X-ray measurements, at first reported the bismuth-copper superconductors to be Aurivillius structures [6], while neutron measurements showed that the true structure of the bismuth oxide layers was quite different [7].

Even the chemical formula for the X-ray structure of the 90K superconductor, given in the paper’s title as Ba₂YCup₂O₉₋ₓ, was uncertain as to the precise number of oxygens, though the oxidation state of the copper ions was the question of crucial interest according to Bednorz and Müller [3]. The formula in the title of the neutron paper was Ba₂YCup₂O₇, now written YBa₂Cu₃O₇. Neutrons further showed how oxygen could be extracted [8, 9], finally destroying superconductivity in YBa₂Cu₃O₆.

1.2. ADVANTAGES OF NEUTRON DIFFRACTION

This is only the most recent example where the extra ‘details’ provided by neutrons proved essential, leading directly to a fuller understanding of the chemistry, and even pointing the way to more interesting materials. The problem with X-rays is that scattering depends on the number of electrons, so light elements are difficult to see in the presence of heavy atoms. Neutrons are scattered by reaction with the nucleus, which can be just as strong for light elements as for heavy elements. Furthermore, X-ray scattering falls off strongly with angle, because of the large size of the atom (the ‘form factor’ effect), and high angle scattering is needed for high spatial resolution of the structure. Neutrons, scattered by the much smaller nucleus, have a form factor almost constant with scattering angle.