Perth IUCr Invited talk (Alan Hewat)

Mr Chairman, Ladies and Gentlemen, ...12 years ago when I was a young postdoc, I was asked at the last minute to take part in a debate on Powders verses Single Crystals at the 1975 IUCR neutron diffraction meeting at Petten. This is of course the home laboratory of Hugo Rietveld, who invented neutron powder diffraction, but he was not there to defend himself. Immediately before I spoke, George Bacon, who had written the bible, Before Rietveld, on neutron diffraction....rose with his lecture notes and said.....
"Gentlemen, I have here the results of 60 years work in crystallography using single crystals"......(tears up the notes)....."and that is powder diffraction !"

That night in my bed, I lay awake thinking of what I should have replied. I should have picked up the pieces and said......
"Now I can do my powder experiment......and Professor Bacon can do his experiment....(dropping them).....when he puts them together again !"

Mr Chairman, let me show you a single crystal. (#2 slide123 SC twins). This material is a perfectly ordinary perovskite oxide of the kind we were using in 1975 for the powder diffraction study of structural transitions. (#1 perovskite T/Ns) Like many other such materials, the symmetry of the material at high temperature, where the crystals are grown, is higher than the symmetry at low temperatures. Therefore, when the crystal cools down, it breaks up into micro-domains of the low symmetry structure. You see that in this case these domains are only about 800 wide. As you can imagine, this is rather common Why should the crystal symmetry be the same at 1000oC when the crystal is grown, as at absolute zero.

Of course, within these micro-domains, the crystal may be perfectly well ordered. Here is a beautiful high resolution electron diffraction image of the structure of such a perovskite. (#1 HREM image of 123 SC). Now here is a high resolution image down the c-axis showing the plane of the domain boundaries. (#2 HREM image down c). You can't see the domain boundaries ? It's not obvious. You must look along the atom planes to see the break in the angle. Here is the same image with the domain boundaries drawn in. (#2 HREM image down c with ruler) What is amusing here is that the planes of heavy atoms continue across the domain boundary, and only the oxygen atom positions are slightly different. The angle between domains is less than 2o. You can imagine that it is not easy to see the difference between domains with conventional crystallography.

Now this kind of crystal presents a problem for conventional crystallography. First of all, it is not always obvious that the 'twinning' exists. The difference between two axes may be less than 1%, and the structure obtained with this 'single crystal' may look perfectly reasonable. Of course one would obtain the average structure, which is the real structure at high temperature.

For powder diffraction, this micro-twinning doesn't make any difference, provided the resolution is sufficient to show the splitting of the lines. and the resolution of powder diffractometers is much better than 1%, and often better than 0.1%. That is why we choose powder diffraction to study structural phase transitions.

Now this rather ordinary perovskite oxide does have one interesting property. It conducts electricity with zero resistance at nearly 100K ! Neutron powder diffraction has been essential for determining the structure of these materials.

All of these beautiful images were taken by Elizabeth Hewat, using the techniques she learned as a student of John Cowley and Alex Moodie. The samples were prepared in the Grenoble CNRS crystallography laboratory of Massimo Marezio by J.J. Capponi.

As you know, there was great excitement this year when the rest of the world realised the importance of the discovery made last year in Zurich, Switzerland of these superconducting copper oxides by George Bednorz and Alex Muller. (#1 slide High Tc titles)....The 98K conductor was quickly discovered after frantic effort in both the US and Japan.

In the middle of March this year, I had a computer message from Ray Young in Atlanta, who was very excited about the crystallography of these materials (#2 Slide RAY). Apparently all the best X-ray crystallographers were in agreement about the structure. (#2 Bayu X-ray structure). It was an oxygen defect perovskite ABO3 with (Ba,Y) in the A-position, ordered along the c-axis as Ba-Ba-Y etc., and Cu in the B-position. All oxygens on the Y-plane were missing, and also some of those on one of the Cu-planes. The theoreticians were very excited about the role of the oxygen deficiency and disorder.

When we received this message from Ray Young, we in Grenoble were feeling very superior, because we had just done the experiment with neutrons, and knew that the disordered X-ray structure was

wrong.. (#1 Hewat to Ray) We sent back a message to Ray to tell him of his error. . (#1 Bayu neutron structure). The structure was not disordered, but contained one dimensional copper oxide chains. It turned out that these chains are essential for superconductivity in the material.

These chains extended along the b-axis, explaining why this was slightly longer than the a-axis. The structure then contains no oxygen octahedra, the most important feature of the perovskite structure. It is however, a perfectly reasonable structure for a cupric oxide. Within the copper oxide plane, each copper has 4 nearly equivalent oxygen neighbours, and two more oxygens much further away, out of the plane. Within the copper oxide chains, again each copper has 4 nearly equal bonds to oxygen, but there is simply no room for further oxygen, which would have to be further away. Then there are large channels running parallel to the CuO chains. This Grenoble work was published in Europhysics Letters (#2 Euro.L. title).

We also reported our results the 8th April at the European Physical Society meeting in Pisa, Italy, and learned there that Jim Jorgensen and the Argonne group had simultaneously obtained the same result using time-of-flight neutron powder diffraction at room temperature. (#2 Argonne ref). Shortly after, many other neutron laboratories reported the same structure, some also confirming our low temperature results.

The important point is not which neutron lab. obtained the result first by a few days, but that all of the neutron powder results were unambiguous, and added essential imformation to the X-ray structure which could not be obtained by any other means. It is also important that the smaller neutron diffraction labs were able to compete with the big labs. For example, the Japanese neutron labs were of course among the first to report the correct 1,2,3 structure.(#2 Japanese work). Bill David and Co. at the new spallation neutron source in England (#2 RAL work) produced the most famous picture of the structure on the front cover of Nature in June. In Russia, the Finnish-Leningrad team obtained very nice results on their reactor based time-of-flight machine. (#2 Russian work). Some of the most careful work was done by Frank Beech, Tony Santoro and Co. at the National Bureau of Standards reactor in Washington. (#2 NBS work) All of these, and many more, neutron powder experiments agreed about the basic structure of the 1,2,3 material.

Of course, it was only right that Peter Fischer et al. at the Zurich neutron lab had been among the first to report on the structure and structural transition in the original La2CuO4 conductor discovered in Zurich. (#2 Fischer paper). The structure of the material discovered by Bednorz and Muller is really very similar to that of the new 100K material. (#2 La2CuO4 structure). In both cases, there are planes of copper oxide with additional oxygen less strongly bonded.

The structural transition in the original La2CuO4 material also breaks up single crystals. When the crystals are grown they are tetragonal, but when they are cooled, the oxygen octahedra tilt against each other and produce a slightly orthorhombic phase. This is the old story for perovskite-type structures. The structural transition temperature decreases when some of the La is replaced by divalent Ba or better Sr, and the superconducting transition temperature increases. The fact that there is a structural instability is very interesting because the BCS theory uses phonons to couple pairs of electrons together in the superconducting state; many of the classical superconductors have structural instabilities.

Recently B. Batlogg at Bell labs showed that the superconducting temperature of La2CuO4. is also changed when the isotope O18 is substituted. This isotope effect, which Batlogg had previously showed not to exist in the 1,2,3 superconductor is the classical test for the influence of phonons. We would really like to replace just one oxygen to see which had the most effect. If the out-of-plane oxygen showed the largest effect, it would indicate that the soft mode responsible for the orthorhombic-tetragonal transition was important. If isotopic replacement of the in-plane oxygen was important, it would indicate that the Cu-O 'breathing mode' was probably involved. Bell labs sent us some of this material, but we found that with their method of oxygen exchange, the heavy isotope apparently replaced oxygen both in and out of the planes.

Neutron powder diffraction has however revealed another exciting feature of the La2CuO4 superconductor. Experiments on the Brookhaven reactor have shown that, at least when the material is oxygen deficient (and not superconducting) there is magnetic ordering. (#2 Brookhaven magnetism) Neutron diffraction is of course the most direct evidence for magnetism, and permits the magnetic structure to be obtained. This is exciting because a strong alternative theory for the new superconductors predicts electron pairing due to spin interaction, rather than phonon coupling.

Unfortunately, despite much effort at ILL and elsewhere, no copper magnetism has yet been found in the 100K superconductor, and there is no isotope effect either.
Of course the 1,2,3 material can be made magnetic by replacing the Y by a magnetic rare earth, and it is interesting to study the interaction of these 'enemy brothers' magnetism and superconductivity. It is known that almost any rare earth can be used to produce a high temperature superconductor. Gadolinium is a suitable magnetic element, but unfortunately, ordinary Gadolinium is very absorbing for neutrons. Very recently the Oak Ridge National laboratory produced an 8g sample of gadolinium isotope xxx substituted

superconductor, and brought it to ILL to determine its magnetic structure at 1.3K. ....

In fact, the weekend before leaving for Australia, we were still doing experiments on superconductors, much to the dismay of our families, on some of the samples which are brought to us by various European and American laboratories.

Clearly, neutron powder diffraction can contribute much more to the study of superconductivity in these materials. Until the neutron powder results were obtained at the end of march, there was much confusion about the oxygen stochiometry of the 100K material, and its effect on superconductivity. It then became clear that although the best material was stochiometric with the formula O7, it was possible to remove oxygen from the linear chains until the formula became O6. (#2 Ba2YCu3O6). The X-ray structure was published in Nature in June by the Grenoble group, and shortly after confirmed by neutron powder diffraction at Argonne, NBS and ILL.

Jim Jorgensen and Co at Argonne have done some beautiful neutron powder experiments on the structure of the O7 material as a function of temperature and oxygen partial pressure. (#2 Argonne O6). They showed an oxygen order-disorder transition above 500oC, with the oxygen within the chains disordered over the two sites along the y- and x-axes, much as in the original X-ray structure of the material. This disordered structure is ideally tetragonal, and remains so until all of the chain oxygen is lost to give the O6 structure.

At ILL Grenoble, we also performed high temperature experiments to complete our earlier low temperature work. We found that even in air at the relatively low temperature of 250oC, the oxygen deficient material could take up oxygen until the O7 formula was obtained i.e. until the chains were completely filled. No oxygen was taken up elsewhere. This means that the material becomes an oxygen conductor above about 250oC, so that the picture of oxygen localised on just two sites is not quite complete. In fact the oxygen must move down the y-axis channels parallel to the CuO chains.

At low temperatures, we had found that there is apparently no structural transition, but it is possible to see some disorder corresponding to the transition to ionic conduction above room temperature. If we plot the thermal Debye-Waller factors as a function of temperature (#2 Bij 0-400K), it is remarkable that the chain oxygen has relatively large displacements perpendicular to the chain. The Debye-Waller factor in these directions is about 1 even near absolute zero, while for all other atoms it is normal at about 0.3. Of course there are rather large errors on these anisotropic temperature factors, but the trend is very clear. As the material is heated, the oxygens within the chains are increasingly displaced toward the parallel tunnels through which they will eventually move. This motion becomes very large above room temperature. (#2 Bij 0-1000K).

If we cool the sample slowly, the displacements decrease normally, but if we quench the sample, we can freeze in some of this disorder.

What does this mean ? Presumably that these chain oxygens are moving in a rather flat potential even at low temperature, and multiple minima are possible. This is normal for an ionic conductor.

What does this have to do with superconductivity ? Perhaps nothing, but the isotope effect is expected for an harmonic oscillator, and there may be a way to explain its absence for such a flat anharmonic potential potential. At the international meeting on superconductivity last month in Trieste, at which for the first time there were large delegations from Russia, China, and India, there were no new superconductors reported, contrary to earlier Press releases, but still as many theories about the new materials as theorists. For the moment, magnetic spin coupling seems to be the favourite, but then how does one explain the low temperature superconductivity in other mixed valence oxides such as BaPbBi-oxide ?

These 'old' ceramic superconductors are being studied with new interest by both neutron powder diffraction, in Grenoble, and by Synchrotron diffraction in Brookhaven and Hambourg. Again there are phase transitions and twinned crystals which make conventional crystallography very difficult.

The new superconductors have in fact been the best thing that has happened for neutron powder diffraction since Rietveld. Our own work at ILL was done on the old D1A machine, which was due to be closed down with the building of our new diffractometers. We now have more user demand than ever. Reactors without modern neutron powder diffractometers have suddenly realised that it is an essential basic technique, and probably we will continue with four powder diffractometers.

It is clear that even the small reactor centers can compete in high user demand areas such as powder diffraction and small angle scattering.