Superconducting ceramics

Oxygen defects and structure

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A FULL understanding of how the properties of the new high-temperature (T_c) superconducting oxides depend on the stoichiometry and the degree of 'doping' with added impurities is probably essential to understand the mechanism of superconductivity in these materials. For example, the roles of factors such as mixed valence effects and the avoidance of instabilities associated with exactly half-filled electron bands are intimately connected with the impurity and oxygen content, and their arrangement in the crystal structure of the oxide. There have been several important recent developments along these lines, for La_2CuO_4 as well as $YBa_2Cu_3O_{7-x}$, including those of Strobel *et al.*[1], Ourmazd *et al.*[2] and David *et al.*[3], who report their new results on pages 306, 308 and 310 of this issue, respectively.

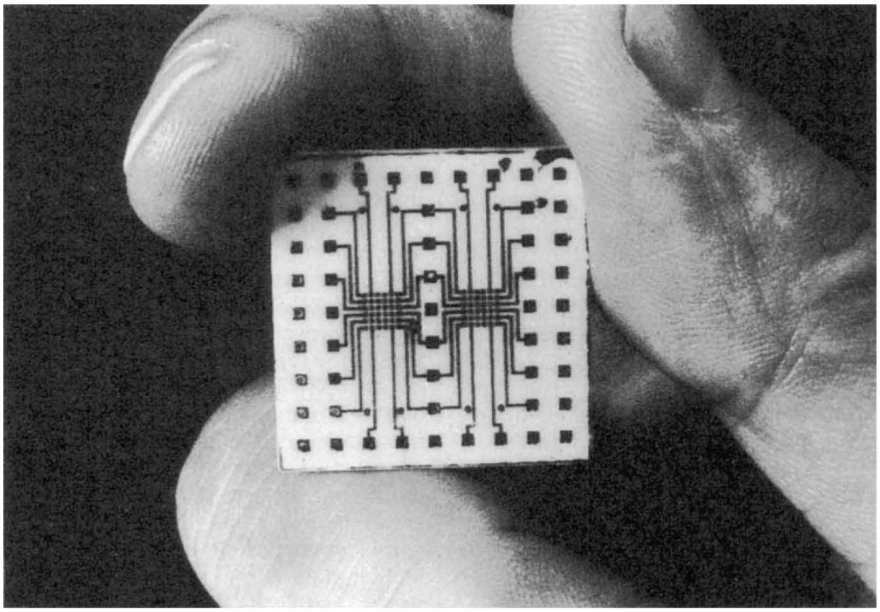
David *et al.*[3] report a determination of the structure of $YBa_2Cu_3O_{7-x}$ from high-resolution neutron powder-diffraction data. This structure has been independently determined by the same technique by at least five other groups[4–8]. The structure is orthorhombic with assigned space group *Pmmm* and may be viewed as a heavily-distorted, oxygen-defective, ordered derivative of a perovskite-type structure. Two-thirds of the copper atoms have four nearest-neighbour oxygens and one, more distant neighbour in a square-pyramidal arrangement, and form a two-dimensional network in the *a–b* planes linked through corner-shared oxygens about 0.03 nm out of the plane. The remaining one-third of the copper atoms have square-planar coordination in the *b–c* planes and form chains linked through corner-shared oxygens along the *b*-axis (see cover of this issue). Thus, low-dimensionality in the copper–oxygen structure, the role of which in high-T_c superconductivity has been debated in connection with the La_2CuO_4-based superconductors, is also a factor here.

A common feature of the structures of both types of high-T_c oxide is the existence of quasi-two-dimensional CuO_2 planes. There seems to be growing evidence, however, implicating the chain-like Cu–O configuration as an important factor in the superconductivity[9–11]. It appears that the removal of oxygen atoms occurs most easily (and reversibly) from these chain sites, causing a substantial deterioration in T_c (even to zero as x approaches unity[10] in $YBa_2Cu_3O_{7-x}$); furthermore, the tetragonal modification of the structure of this oxide may be a consequence of the destruction of the long-range chain-like structure by disordering as well as by oxygen removal[9–11]. Strobel *et al.*[1] in their paper in this issue report a systematic study on the effect of oxygen loss, on the valence state of copper, and its relation to processing conditions. The significance of one-dimensional Cu–O structures has been pointed out by Mattheiss and Hamann (personal communication) based on their band-structure calculations for a related structure for $YBa_2Cu_3O_{7-x}$.

The one-dimensional Cu–O chain structure, inferred from neutron-diffraction data as discussed above, has also been observed directly in atomic-resolution, electron-microscope images of $YBa_2Cu_3O_{7-x}$ by Ourmazd *et al.*[2] in this issue, that also show numerous planar defects, which presumably result from the accommodation of the structure to deviations from ideal oxygen stochiometry. This work clearly shows that one cannot naively assume that oxygen deficiency is simply accommodated by the creation of point defects alone. In their enthusiasm for these planar defects, Ourmazd *et al.* even make the novel suggestion that they may contribute to superconductivity by an enhancement of electron localization.

Two recent experiments on La_2CuO_{4-y}, related to the first high-T_c superconductors, $La_{2-x}A_xCuO_{4-y}$ (A=Ba, Sr...), are likely to have a great impact on our thinking about these materials. According to simple valence-counting arguments (and expensive electronic structure calculations) the ground state of the CuO_2 planes in La_2CuO_4 should be insulating and display some kind of long-range order: antiferromagetism if coulombic interactions dominate; or a lattice distortion if phonon coupling is more important. Working at the High Flux Beam Reactor at Brookhaven National Laboratory, several groups found that La_2CuO_{4-y} is antiferromagnetic, but only if the oxygen deficiency is greater than a few per cent[12–14]. At about the same time, workers from laboratories in Grenoble found that La_2CuO_{4-y} is superconducting below about 38 K, provided that y is kept as small as possible (J. Beille *et al.*, personal communication).

The two results are not inconsistent as oxygen defects control the density of electrons in the CuO_2 planes. Antiferromagnetism occurs with an average of one electron per copper atom, whereas superconductivity requires a smaller number. The puzzle is that La_2CuO_4 is antiferromagnetic when non-stoichiometric in



ART meets physics: the picture shows a circuit board made by scientists at IBM's Yorktown Heights laboratory with a thin film of Y–Ba–Cu–O superconductor using a method they call spray painting. This method, in fact a well-established technique more properly called plasma spraying, involves ionizing a jet of powdered oxides in an electric arc just above the substrate surface. The plasma condenses to give a strip a few centimetres wide and a few micrometres deep which is then annealed. The method can be used to coat large and complicated surfaces with continuous films for magnetic-field shielding or to give superconducting wires as shown in the picture. The thickness of the polycrystalline film can be varied to suit the application. The device shown, made by spraying through a template, is typical of the type that would be used to give superconducting links between chips in a computer cooled in liquid nitrogen. □