Control of copper valence in $Bi_2Sr_{2-x}CaCu_2O_8$

SIR—The recent reports[1,2] of superconductivity in the system Bi–Sr–Ca–Cu–O have stimulated a great deal of interest, not least because of the relative ease with which these materials might be fabricated into useful forms. According to Chippindale et al.[3], there are two superconducting phases in the system, with compositions, determined by high-resolution X-ray emission analysis[4], of $Bi_2(Sr,Ca)_{2.66}Cu_2O_x$

Idealized structure of $Bi_2Sr_{2-x}CaCu_2O_8$.
●, Bi; ○,Cu; ⊕,Sr; ⊗,Ca.
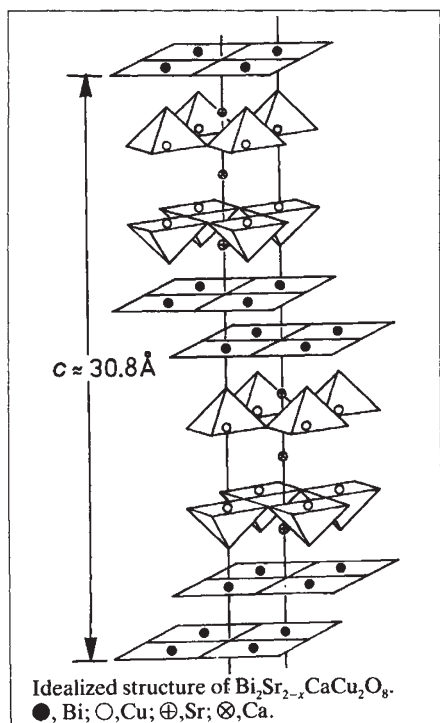
and $Bi_2(Sr,Ca)_{1.5}CuO_x$, respectively. Here we are primarily concerned with the first of these phases. The structure of this phase has recently been reported[5,6], and indicates a chemical composition that is at variance with the analytical results. According to a combined X-ray and neutron powder study by Bordet et al.[5], the composition is $Bi_2Sr_2CaCu_2O_8$ and the space group of the orthorhombic cell ($a=5.401$, $b=5.401$, $c=30.83$Å) is Fmmm (see figure). The structure reported by Subramanian et al.[6] is broadly similar, although several of the oxygen atoms are not located. It is assigned the composition $Bi_2Sr_2CaCu_2O_{8+y}$ and the orthorhombic space group ($a=5.399$, $b=5.414$, $c=30.904$Å) Amma.

Under normal circumstances, the composition obtained by diffraction methods would be regarded as definitive, but there are several reasons why the chemical results should not be ignored. First, they are corroborated by several other determinations by electron microprobe analysis, including those of Takagi et al.[7], who obtained Bi:Sr:Ca:Cu ratios corresponding to $Bi_2Sr_{1.4}CaCu_2O_x$, and Takayama-Muromachi et al. (preprint), who found

the composition $Bi_2(Sr,Ca)_{2.50}Cu_2O_x$. Zandbergen et al.[8] report similar findings. Second, the two structure determinations of the phase are of modest quality and in entirely different space groups. Neither takes into account the modulation of the structure that leads to an approximately 5-fold incommensurate superlattice along the b-axis. The Bordet et al. structure[5] appears to be the most reliable in that all of the atoms, including oxygen, have been located. It does, however, have the curious feature that the composition of the structural model, $Bi_2Sr_2CaCu_2O_8$, would require all of the copper to be present in the +2 oxidation state, even though their bond-strength calculations point to a mean oxidation state of +2.335. The latter is approximately what would be expected by analogy with other superconducting oxides such as $YBa_2Cu_3O_{7-x}$ (ref. 9). In the work of Subramanian et al.[6] the oxygen atoms in the bismuth layers were not located and the composition must therefore be regarded as suspect, but the mean oxidation state of the copper, obtained by bulk chemical analysis, was again found to be approximately +2.33.

How can the conflicting models obtained by analytical and diffraction methods be reconciled? If we assume that the structure reported by Bordet et al.[5] is essentially correct, we can obtain agreement with the analytical data of ref. 3 simply by removing 16 per cent of the strontium atoms from their model. Such a minor error in the structure could easily be accommodated by a slightly higher temperature factor, especially in a structure that is known to have additional subtlety that is not in the model. Removal of this small fraction of strontium yields a composition of $Bi_2Sr_{1.68}CaCu_2O_8$, in excellent agreement with that reported in ref. 3, which is $Bi_2Sr_{1.67}Ca_{0.99}Cu_2O_x$ when the observed Sr/Ca ratio (1.69) is taken into account. This minor change may seem of little importance, but its real significance lies in the fact that it brings the mean oxidation state of the copper up to exactly +2.33, as observed and, indeed, expected. Furthermore, the presence of defects in the strontium layers may be related to the observed modulation of the structure along b.

The essence of our proposed model is that the oxidation of Cu^{2+} in $Bi_2Sr_2CaCu_2O_8$ is controlled by depleting the strontium content according to the general formula $Bi_2Sr_{2-x}CaCu_2O_8$. This is in contrast to the systems $(La_{2-x}Ba_x)CuO_4$ and $YBa_2Cu_3O_{7-x}$, in which the copper oxidation state is determined by substitutional defects and oxygen defects, respectively. It is also likely that a similar mechanism operates in the second bis-

muth superconductor, where the analytical data would be consistent with the formulation $Bi_2(Sr,Ca)_{2-x}CuO_6$, rather than $Bi_2(Sr,Ca)_2CuO_{6+x}$, a possibility that has already been mooted[10].

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Superconductivity and microwave absorption

SIR—Recently, Sastry et al.[1] suggested that the low-field electron spin resonance (ESR) signal of $YBa_2Cu_3O_{7-x}$ superconductors observed with an X-band spectrometer could be attributed to a large zero-field splitting arising from dimerization of electrons on copper pairs in adjacent octahedra. But our work and that of others[2,3] clearly indicate that the low-field signal is not caused by a resonant effect.

Our work has been done on three ESR spectrometers: S-band (microwave resonance frequency 2.40 GHz); X-band (IBM-Bruker ESR200 at 9.45 GHz); and Q-band (23.0 GHz). For each instrument, field scans through true zero magnetic field were ensured by special circuits. We prepared superconductors from ultra-pure Y_2O_3, $BaCO_3$ and CuO according to the standard solid-state procedure[4]. The transition temperature is 93 K, with a width less than 2 K.

The figure shows the ESR spectrum obtained from both increasing- and decreasing-field scans at 77 K in the X-band instrument. The breadth of the hysteresis is 5 G, centred at −2 G in the forward direction and 0 G in the backward direction. The breadth of the hysteresis effect depends on the field applied while the sample was cooled through the transition temperature. The spectra obtained with both the lower and higher frequencies are almost identical to those obtained with the X-band instrument. The results at 2.40 GHz are shown in b in the figure. Note that the lower frequency is insufficient to induce a transition between

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