High-T_c Superconductors

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PREFACE

In the past two years conferences on superconductivity have been characterized by the attendance of hundreds of scientists. Consequently, the organizers were forced to schedule numerous parallel sessions and poster presentations with an almost unsurveyable amount of information. It was, therefore, felt that a more informal get-together, providing ample time for a thourough discussion of some topics of current interest in high-temperature superconductivity, was timely and benefitial for leading scientists as well as for newcomers in the field.

The present volume contains the majority of papers presented at the International Discussion Meeting on High-T_c Superconductors held at the Mauterndorf Castle in the Austrian Alps from February 7 to 11, 1988. Each subject was introduced in review form by a few invited speakers and then discussed together with the contributed poster presentations. These discussion sessions chaired by selected scientists turned out to be the highlights of the meeting, not only because all the participants truly appreciated the possibility of an information exchange, but mainly because of the magnificent job done by the discussion chairmen, John A. Mydosh (Leiden), Martin Peter (Geneva) and Ken E. Gray (Argonne). First results on the just discovered Bi-superconductors and the clarification of electron resonance experiments on (123)-compounds should be mentioned in particular.

The relaxed atomosphere favoring free discussions was certainly promoted by the surroundings offered in the Mauterndorf Castle, which dates back to 1253. Poster presentations and a conference banquet in historic knight's halls are certainly not found everyday in conference routines. Special thanks are due to the staff of the castle and the State of Salzburg, which offered the conference location and provided financial support. Furthermore, I wish to acknowledge the encouragement of Prof.Dr.Hans Tuppy, Minister of Science and Research, who also attended to open the meeting, the support of the Federal Ministry of Science and Research, the Austrian Physical Society and the Atomic Institute of the Austrian Universities. The invaluable help of the staff members Dr.Erwin Seidl, Dr.Franz M. Sauerzopf, Mr.Hans Niedermaier, Mrs.Ilse Futterer and, in particular, Mrs.Brigitta Buchberger as well as of my graduate students Trixi Vlcek, Marcus Frischherz, Peter Gregshammer, Michael Wacenovsky and Heinrich Wiesinger are gratefully acknowledged.

Finally, I wish to thank Plenum for the smooth cooperation during the production of this book, Brigitta Buchberger for her patience with the typing of numerous papers and my wife Ann for her help with the editing of this book.

Harald W. Weber

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SECTION 1: OVERVIEW

THE SOLID STATE CHEMISTRY OF MIXED VALENCE COPPER OXIDE HIGH T_c SUPERCONDUCTORS

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INTRODUCTION

The recent investigations of superconductivity in ternary or pseudo ternary copper oxides recently performed by numerous staffs all over the world, show that up to the present, only two structural families belonging to the La_2CuO_4 and $YBa_2Cu_3O_7$ types, exhibit high critical temperatures, i.e. greater than 30K. The main factors which govern the superconducting properties are discussed here in a first point. $YBa_2Cu_3O_{7-\delta}$, appears as most fascinating owing to its high T_c (92K), but also very complex owing to its large possible oxygen deviation from stoichiometry. Its structural evolution versus oxygen non stoichiometry involving extended defects is presented in connection with its superconducting properties. The substitution of copper by a magnetic element, iron, very recently performed is finally presented here, taking into account the oxygen stoichiometry in the oxides $YBa_2Cu_{3-x}Fe_xO_7$.

La_2CuO_4-TYPE AND $YBa_2Cu_3O_{7-\delta}$-TYPE, TWO LOW DIMENSIONAL SUPERCONDUCTORS

The formal mixed valence of copper Cu(II)-Cu(III) necessary for a hole delocalization, i.e. for the existence of metallic or semi-metallic properties of copper oxides, is not sufficient for the appearance of superconductivity. It is now well established that mixed valence copper oxides such as $La_4BaCu_5O_{12+\delta}$[1a] or $La_{8-x}Sr_xCu_8O_{20}$[1b] do not exhibit any superconductivity in spite of their metallic conductivity contrary to the oxides $La_{2-x}A_xCuO_{4-y}$ (A = Ba, Sr, Ca)[1a,2] and $YBa_2Cu_3O_{7-\delta}$[1a,3]. These latter oxides are characterized by a layered structure. The "40K"-La_2CuO_4-type superconductor exhibits indeed a K_2NiF_4 structure **(Fig. 1a)** built up from SrO-type innsulating layers intergrown with single oxygen deficient superconducting perovskite layers. In the same way the "92K" $YBa_2Cu_3O_7$ superconductor has its structure **(Fig. 1b)** formed of triple infinite $[Cu_3O_8]_\infty$ layers built up of corner-sharing CuO_5 pyramids and CuO_4 square planar groups, whose cohesion is ensured by yttrium planes. This low dimensionality of the structure appears as a second necessary factor for superconductivity as very early pointed out by Labbé and Bok[4].

The question which can be set out deals with the role of Cu(III) content in the superconducting properties of these low-dimensional oxides. The evolution of the critical temperature versus oxygen non-stoichiometry δ in $YBa_2Cu_3O_{7-\delta}$ established by several authors[5a,b-7] shows that T_c decreases as Cu(III) content decreases (Fig. 2). However a contradition appears for $\delta \geq 0.50$ if one takes only into consideration the classical behavior of copper : $YBa_2Cu_3^{II}O_{6.50}$ would only contain Cu(II) from the charge balance and should not be a superconductor. The explanation to this phenomenon takes its origin in the particular structure of $YBa_2Cu_3O_{7-\delta}$ which will be in fact an intergrowth between the $YBa_2Cu_3O_7$ structure (Fig. 1b) and the $YBa_2Cu_3O_6$ one (Fig. 3).

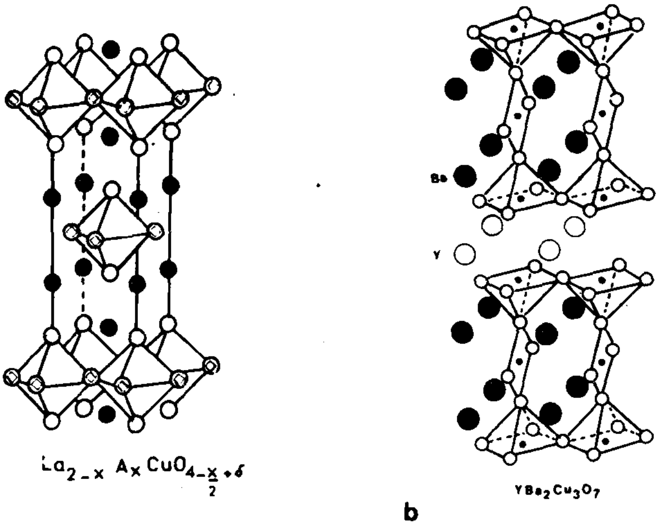


Fig. 1. Crystal structure of the oxides K_2NiF_4-type (a), $YBa_2Cu_3O_7$-type (b)

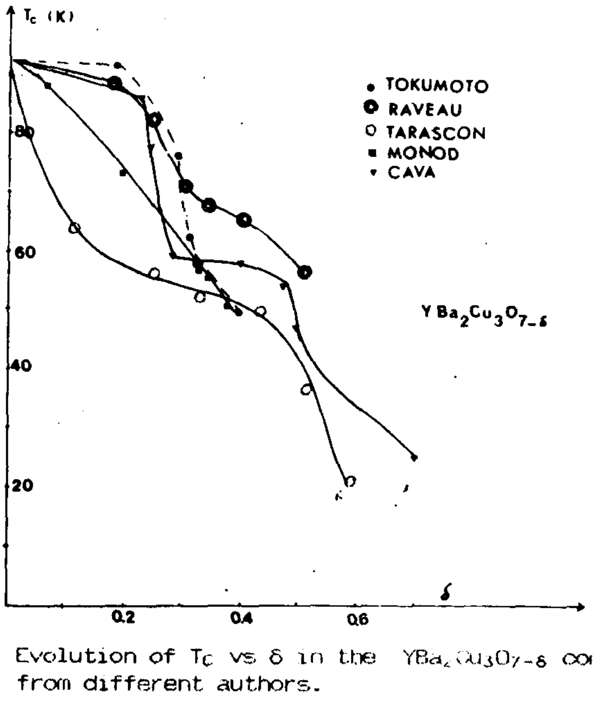
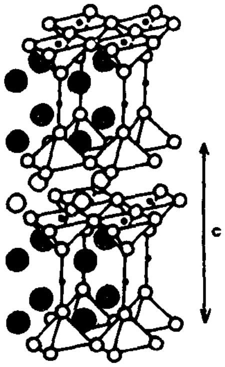


Fig. 2. Evolution of T_c vs δ in the $YBa_2Cu_3O_{7-\delta}$ compounds, from different authors.



$YBa_2Cu_3O_6$

Fig. 3. Crystal structure of $YBa_2Cu_3O_6$.

Consequently, whatever δ may be, different from 0 and 1, one observes a disproportionation of Cu(II) into Cu(III) and Cu(I) leading to Cu(II)-Cu(III) superconducting regions and Cu(II)-Cu(I) insulating domains coexisting in the same crystal. Contrary to $YBa_2Cu_3O_{7-\delta}$, the La_2CuO_4-type oxides will not present this disproportionation: the formation of anionic vacancies, according to the formulation La_2CuO_{4-y} does not lead to a linear coordination of copper, characteristic of Cu(I), but either to a pyramidal or to a square planar coordination compatible with Cu(II) and Cu(III). The observation of noticeable amounts of Cu(I) in $YBa_2Cu_3O_{7-\delta}$ by X-ray absorption spectroscopy[8,9], whereas no Cu(I) was detected by Bianconni et al.[1b] in La_2CuO_4-type oxides, is in agreement with this point of view.

Superconductivity observed for La_2CuO_4[1a-1b] corresponds to a particular behaviour of this structure. The oxide La_2CuO_4, prepared by annealing in air or under an oxygen flow, is only a surface superconductor, due to the existence of Schottky defects in the normal semi-conductor $La_{2-2\epsilon}Cu_{1-\epsilon}O_{4-4\epsilon}$, whose surface is then more easily oxidized by long time annealing, leading to the limiting formulation $La_{2-2\epsilon}Cu_{1-\epsilon}O_4$. On the opposite the bulk superconductor obtained by annealing under high oxygen pressure the compound corresponding to an excess of CuO, can be formulated $La_{1.95}CuO_4$, and thus has a hole concentration i.e. a Cu(III) content close to that of $La_{1.85}Sr_{0.15}CuO_4$, in agreement with its similar value of T_c (37K).

STRUCTURAL EVOLUTION OF $YBa_2Cu_3O_{7-\delta}$ VERSUS OXYGEN STOICHIOMETRY

The ability of $YBa_2Cu_3O_{7-\delta}$ to adopt a large oxygen non stoichiometry, $0 \leq x \leq 1$, is now a well known feature. Several studies showed that the oxygen content and/or the symmetry (orthorhombic or tetragonal) have a direct influence on the superconducting properties of these oxides, corresponding to a decrease of the T_c vs δ[5a,b-7]. However, if such a mean effect is observed, the values of the parameters differ from one author to the other, owing to the accuracy of the oxygen content measurement and the thermal treatment. Moreover, these overall results do not take into account the real state of the matrix. In that way, the structures of the limiting compounds, $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$, were well characterized as well by X-ray single crystal as by neutron diffraction techniques [1a,1b,10]. The first one ($0 \le \delta \le 0.2$) was systematically investigated by means of electron diffraction and high resolution microscopy by several groups[1b,17,18] showing local variation of the oxygen stoichiometry, twins and oriented domains and various extended defects. On the opposite few studies were performed near the composition $YBa_2Cu_3O_6$[1b]. The electron diffraction investigation of numerous particles in the $YBa_2Cu_3O_6$ matrix, corresponding to samples with nominal compositions $\delta = 1$ obtained from different thermal treatments (argon, vacuum, sealed tube with zirconium) showed to us that all the phases exhibit a large part of amorphous or bad crystallized grains, besides the tetragonal crystals which can be picked up for X-ray or H.R.E.M. studies. This feature can indeed be correlated with an inhomogeneous removing of the oxygen atoms from one grain to the other, depending on the nature of the precursor $YBa_2Cu_3O_{7-\delta}$. Moreover, the E.D. patterns of some of these crystals exhibit extra spots corresponding to a tetragonal $2a\sqrt{2} \times 2a\sqrt{2}$ superstructure (Fig. 4). Such a feature can be correlated to the existence of residual oxygens in the matrix, rearranged in a short range order, corresponding to a well defined composition such as $\delta = 0.875$ or $\delta = 0.75$. Such an assumption is reinforced by the behavior of those crystals under the electron beam : the extra spots quickly disappear to give the tetragonal subcell spots ($a \times a$), after a loss of the residual oxygen. Unfortunatly, this phenomenon prevents accurate HREM images to be recorded, which would help to understand this ordering.

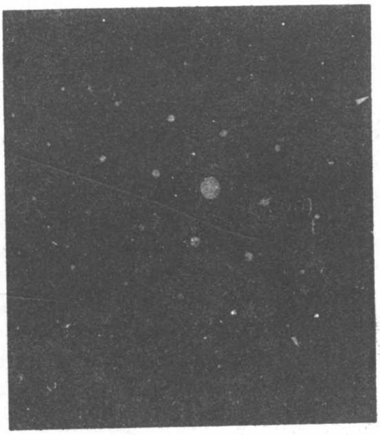


Fig. 4. [001] electron diffraction pattern, brighter dots correspond to the tetragonal subcell and the smaller ones to a $2a\sqrt{2} \times 2a\sqrt{2}$ superstructure.

More difficult, because more complex, is the understanding of the intermediate compositions, i.e., $0.2 < \delta < 0.7$, where the thermal treatments are, once more, of high significance (particularly under reduction or reoxidization way of preparation). For instance, "mixed" crystals, partly orthorhombic partly tetragonal, were observed for a sample of nominal composition $YBa_2Cu_3O_{6.7}$ obtained by reoxidation of $YBa_2Cu_3O_6$ (Fig. 5) ; they appear as half twinned on the image. Such crystals are assumed to be formed of the intercalation of oxygen atoms in a well crystallized $YBa_2Cu_3O_6$ matrix. For the same mixed composition other particles appear as "polycrystalline", as shown on the E.D. pattern and image in Fig.6. Such a feature is correlated to local recrystallisations in an amorphous matrix of the reduced sample $YBa_2Cu_3O_6$, reduced and reoxidized particles exhibiting exactly the same plate-like morphology.

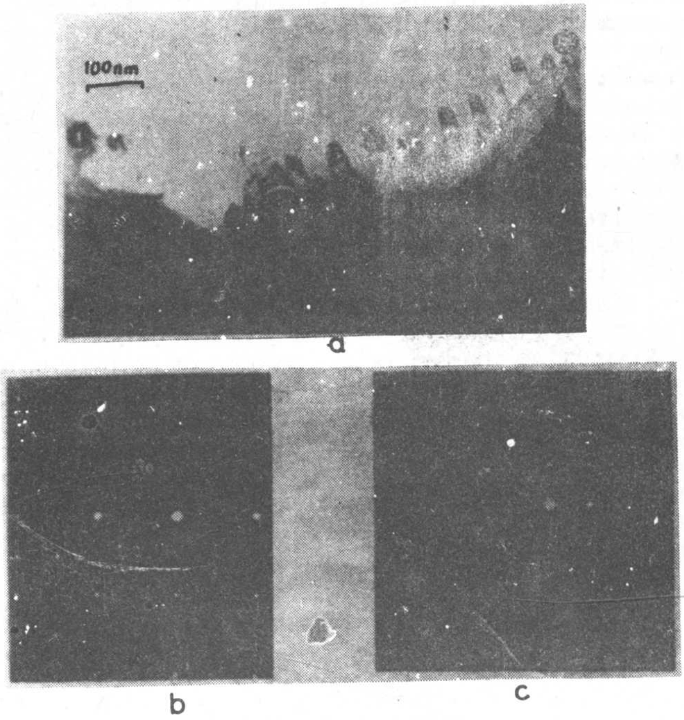


Fig. 5. Low resolution image and corresponding SAED patterns of mixed tetragonal (1-b), orthorhombic (2-c) crystals.

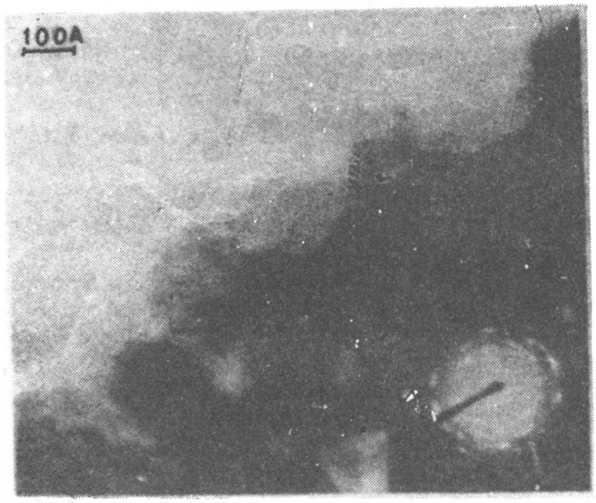


Fig. 6. Low resolution image and ED pattern of a polycrystalline particle.

$YBa_2Cu_3O_{6.5}$ is an other interesting example of the structural evolution of these oxides with their "thermal history". Two sorts of samples must be distinguished : tetragonal semiconducting samples obtained by quenching the orthorhombic superconductor $YBa_2Cu_3O_{6.9}$ in air from 950°C to room temperature and the orthorhombic form obtained by reoxidation of the oxide $YBa_2Cu_3O_6$ at low temperature. The powder neutron diffraction study showed that the crystalline part of the "tetragonal" sample corresponds to $\delta = 0.75$ and that the 0.25 oxygen atoms are statistically distributed in the plane of Cu(1), between the barium atoms (Fig. 7) ; however the important background and the abnormally high values of some anisotropic thermal parameters suggest the existence of an amorphous part in the matrix and some inhomogeneities in the crystalline part. The electron diffraction and HREM studies carried out in order to understand these features revealed, besides well crystallized grains, systematically coated with an amorphous barium rich layer, the existence of highly disturbed crystals, partly polycrystalline states and streaks along c ; moreover careful examination of the particles along [001] showed that the matrix is composed of both true tetragonal crystals and orthorhombic ones ; such phenomena which suggest indeed local variations of the oxygen content were confirmed by the HREM images[15]. Such results support the hypothesis of disproportionation of Cu(II) into Cu(III) and Cu(I) leading to the coexistence in the matrix of both superconducting (Cu(II)-Cu(III)) and "insulating" (Cu(II)-Cu(I)) regions according to the formulation $YBa_2(Cu_2^{II}Cu^{III}O_7)_{0.25}(Cu_2^{II}Cu^{I}O_6)_{0.75}$.

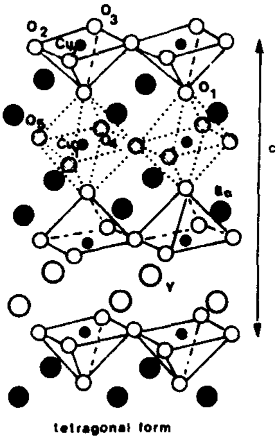


Fig. 7. Crystal structure of the tetragonal oxide $YBa_2Cu_3O_{6.25}$

The HREM study of the orthorhombic form of nominal composition $YBa_2Cu_3O_{6.60}$ carried out in collaboration with Tarascon[11] is also in agreement with this disproportionation of Cu(II). Moreover systematical modulations (2a × b) appear in the contrast of the [001] HREM images (Fig. 8a) ; they can be easily explained by an ordering of the oxygen vacancies (Fig. 8b). Whereas in other samples, some crystals show a × 2b supercells (Fig. 8c, d) witness of a complete ordering all over the crystal.