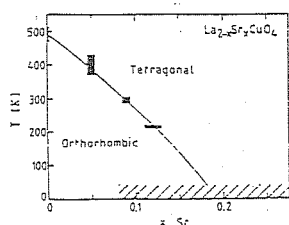


07.3-1 PHASE DIAGRAM OF THE TETRAGONAL TO ORTHORHOMBIC STRUCTURAL TRANSITION IN  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ . By R. Moret, J.P. Pouget and R. Comes, Laboratoire de Physique des Solides, Université Paris Sud, Orsay, France and G. Collin, UA 200, Université René Descartes, Paris, France.

The relation between structural and superconducting instabilities is considered to play a crucial role in the behaviour of the new high  $T_c$  superconductors. In the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  materials it is usually admitted that the effect of Sr alloying to La is to suppress the orthorhombic distortion present in  $\text{La}_2\text{CuO}_4$  and to stabilize the tetragonal phase which is superconducting.

We report here an X-ray scattering study of the structural phase diagram of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ . For  $x = 0.12$  a low  $T$  single crystal study reveals a tetragonal to orthorhombic transition at  $T_{T-O} = 215 \pm 5$  K. The intensity of the associated superstructure reflections and the orthorhombic distortion ( $c - a$ ) (space group  $Cmca$ ) were measured down to 12 K. Precursor diffuse scattering is observed up to room temperature and it is quasi-isotropic. Supplementary powder diffraction data for  $x = 0, 0.05$  and  $0.09$  allow to construct a phase diagram of the tetragonal to orthorhombic distortion (see figure). From this result one can conclude that superconductivity (observed in the hatched region) coexists with the orthorhombic distortion in a broad concentration range, in contrast with previous hypotheses.



07.3-2 HIGH RESOLUTION SYNCHROTRON X-RAY STUDY OF  $\text{La}_{2-x}\text{M}_x\text{CuO}_{4-y}$  ( $M = \text{Ba}, \text{Sr}$ ). by S. C. Moss,\* K. Forster Physics Department, University of Houston, Houston, TX 77004, USA; J. D. Axe, H. You, D. Hohlwein,\*\* D. E. Cox, National Synchrotron Light Source, Brookhaven National Laboratory,\*\*\* Upton, NY 11973, USA; P. H. Hor, R. L. Ming and C. W. Chu, Physics Department, University of Houston, Houston, TX 77004, USA.

High resolution X-ray diffraction of  $\text{La}_{2-x}\text{M}_x\text{CuO}_{4-y}$  ( $M = \text{Ba}, \text{Sr}$ ) reveals two macroscopically segregated phases of the  $\text{K}_2\text{NiF}_4$ -type with nearly identical lattice parameters. In the Sr-substituted material the minor phase shows considerably broader Bragg peaks than the major phase and it occurs in substantial amounts. The two phases are associated with phase separation within a nominally single phase field and are presumably sensitive to oxygen and/or thermal treatment. In a detailed study of  $\text{La}_{1.8}\text{Ba}_{0.2}\text{CuO}_{4-y}$ , several peaks showed additional broadening on cooling. This broadening is consistent with a small spontaneous monoclinic distortion, with an onset temperature of  $\sim 150$  K, which is possibly relevant to the superconducting properties. Small single crystals within the powder aggregate are also studied and show a similar two-phase constituency and a resolvable peak splitting at low temperature.

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07.3-3 NEUTRON AND SYNCHROTRON X-RAY POWDER STUDIES OF A HIGH IONIC CONDUCTOR SYSTEM:  $\text{Li}_{1+x}\text{Ti}_{2-x}\text{In}_x\text{P}_3\text{O}_{12}$ .

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It was recently reported that  $\text{Li}_{1+x}\text{Ti}_{2-x}\text{In}_x\text{P}_3\text{O}_{12}$  solid solutions exhibit high ionic conductivity. This conductivity increases rapidly with increasing values of  $x$ . Arrhenius plots of  $\log \sigma T(x)$  versus the reciprocal of the absolute temperature show three extrema,  $2 \times 10^{-2}$ ,  $2 \times 10^{-3}$  and  $8 \times 10^{-3} (\text{Kcm})^{-1}$  for  $x = 0.35, 1.0$  and  $1.8$ , respectively. It was also found that, depending on the substitution parameter  $x$ , the compounds in this solid solution adopt three structure types, corresponding to three different phases: Phase I is in the region  $0 \leq x \leq 0.4$ , phase II in  $0.4 < x \leq 1.0$  and Phase III in  $1.0 < x \leq 2.0$ . The  $x$  values corresponding to the maximum and minimum conductivities coincide approximately with phase transition boundaries.

In this paper results of our efforts to correlate structural changes with conductivity behaviour are presented: a) Single crystal structure studies of  $\text{Li}_{1+x}\text{Ti}_{2-x}\text{In}_x\text{P}_3\text{O}_{12}$  compounds with  $x = 0.0, 0.06, 1.0, 1.8$  and  $2.0$  indicate that structure framework of compounds in phase I is an  $R\bar{3}c$ , Nasicon-type structure. Further insertion of trivalent  $\text{In}^{3+}$  ions induces much more complicated structural changes: compounds in phases II and III are found to be orthorhombic,  $Pbca$ , and monoclinic,  $P2_1/n$ , respectively. Crystal structures in phases I, II and III, and their relationships, are described.

b) Neutron powder refinements of highly conducting, polycrystalline samples with nominal compositions  $x = 0.25, 0.40$  and  $0.45$  indicate that lithiums in the large eight-coordinated sites are in a highly disordered configuration, occupying only 6% of the site capacity, while the low energy octahedral sites are 95% filled. Such a site distribution, which is unfavorable for fast ion diffusion, may change in the highly conducting state: transfer of Li ions from octahedral sites into the large cavities is therefore expected at high temperature. Results of studies of site occupancies and structural changes as a function of temperature, at 40, 200, 600 and 800 K, along with electrical properties will be discussed.

c) Neutron studies have also suggested the existence of a parasitic phase in the  $\text{Li}_{1+x}\text{Ti}_{2-x}\text{In}_x\text{P}_3\text{O}_{12}$  solid solution. This phase could not, however, be readily identified. Due its exceptionally high resolution a synchrotron x-ray diffraction pattern of  $\text{Li}_{1.25}\text{Ti}_{1.75}\text{In}_{0.25}\text{P}_3\text{O}_{12}$  shows 26 extra reflections, well resolved from the expected lines. Rietveld refinement applied to the x-ray pattern confirms a neutron observation that the observed Ti/In ratio is substantially lower than it should be according to the chemical analysis. These extra reflections are indexed, and a space group and a solution of the crystal structure of this unwanted phase are proposed.