07.3-1 PHASE DIAGRAM OF THE TETRAGONAL TO ORTHO-
ROMBOEDRIC STRUCTURAL TRANSITION IN La$_{2}$Sr$_{2}$CuO$_{4}$
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The relation between structural and superconducting inst-
bilities is considered to play a crucial role in the
behaviour of the new high Tc superconductors. In the
La$_{2}$Sr$_{2}$CuO$_{4}$ materials it is usually admitted that
the effort of Sr alloying to La is to suppress the orthorhom-
bic distortion present in LaCuO$_{2}$ and to stabilize the
tetragonal phase which is superconducting.

We report here an x-ray scattering study of the struc-
tural phase diagram of La$_{2}$Sr$_{2}$CuO$_{4}$. For x = 0.12 a low T
single crystal study reveals a tetragonal to orthorhombic
transition at T$_{c}$ = 215 ± 5 K. The intensity of the asso-
ciated 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 = 0.05 and 0.09 allow to
construct a phase diagram of the tetragonal to orthorho-
bmic distortion (see figure). From this result one can
conclude that superconductivity (observed in the bated
region) coexists with the orthorhombic distortion in
a broad concomitance range, in contrast with previous
hypotheses.

07.3-2 HIGH RESOLUTION SYNCHROTRON X-RAY STUDY OF
La$_{2}$Sr$_{2}$CuO$_{4}$
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High resolution x-ray diffraction of La$_{2}$Sr$_{2}$CuO$_{4}$
(M = Ba, Sr) reveals two macroscopically segregated
phases of the ortho-II 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 La$_{1.98}$Sr$_{0.02}$CuO$_{4}$, several peaks showed
additional broadening on cooling. This broadening is
consistent with a small spontaneous monoclinic
distortion, with an onset temperature of ~150K, 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: Li$_{1+}^{+}$Ti$_{1-}^{3+}$In$_{x}$P$_{2}$O$_{7}$
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It was recently reported that Li$_{1+}^{+}$Ti$_{1-}^{3+}$In$_{x}$P$_{2}$O$_{7}$ solid
solutions exhibit high ionic conductivity. This conduc-
tivity increases rapidly with increasing values of x,
Armstrong plots of log e(1/|x|) versus the reciprocal of
the absolute temperature show three extrema, 2x*10$^{-2}$,
3x*10$^{-6}$ and 8x*10$^{-3}$ (amm) 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 < x < 0.4,
Phase II in 0.4 < x < 1.0 and Phase III in 1.0 < x < 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 struc-
tural changes with conductivity behaviour are presented:
a) Single crystal structure studies of Li$_{1+}^{+}$Ti$_{1-}^{3+}$In$_{x}$P$_{2}$O$_{7}$ compounds with x = 0.6, 0.9, 1.0,
1.8 and 2.0 indicate that structure framework of com-
pounds in phase I is an $A_B$, Nasicon-type structure.

Further insertion of trivalent 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,
polyocrystalline samples with nominal compositions
x = 0.25, 0.40 and 0.95 indicate that lithium in the
large eight-coordinated sites are in a highly disordered
configuration, occupying only 65% of the site capacity,
while the low energy octahedral sites are 95% filled.

Such a site distribution, which is unfavorable for fast
ionic diffusion, may change in the highly conducting
state: transfer of Li ions from octahedral sites into
the large cavities is therefore expected at high tem-
perature. 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 Li$_{1+}^{+}$Ti$_{1-}^{3+}$In$_{x}$P$_{2}$O$_{7}$ solid
solution. This phase could not, however, be readily
identified. Due its exceptionally high resolution a
synchrotron x-ray diffraction pattern of
Li$_{1.25}$Ti$_{1.75}$In$_{0.25}$P$_{2}$O$_{7}$ shows 26 extra reflections, well
resolved from the expected lines. Rietveld refinement
applied to the x-ray pattern confirms a neutron observa-
tion 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.