

**MS10.06.03 THE STRUCTURAL PHASE DIAGRAM OF THE MAGNETORESISTIVE OXIDE  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$ ; RELATIONSHIP TO MAGNETIC AND TRANSPORT PROPERTIES.** D. N. Argyriou, Material Science Division, Argonne National Laboratory, Argonne, IL 60439

The structural phase diagram of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$  has been constructed as a function of both Sr doping ( $0 \leq x \leq 0.225$ ) and oxygen partial pressure during synthesis ( $2.1 \times 10^{-4} \text{ atm} \leq P(\text{O}_2) \leq 1 \text{ atm}$ ). The phase diagram contains a rhombohedral phase ( $R\bar{3}c$ ), an orthorhombic phase ( $Pbmm$ ), and a monoclinic phase ( $P2_1/c$ ). For a given doping level  $x$ , decreasing  $P(\text{O}_2)$  yields smaller cation defect concentrations and consequently a reduction of the average Mn oxidation state. The orthorhombic and monoclinic phases synthesized under low  $P(\text{O}_2)$  exhibit a cooperative Jahn-Teller distortion of the  $\text{MnO}_6$  octahedra, consistent with a high  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratio. For the  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$  system a strong correlation is observed between structural and transport properties; orthorhombic and monoclinic samples are nonmetallic, while rhombohedral samples exhibit a temperature-dependent nonmetal-metal transition at a temperature close to the Curie temperature. Magnetoresistance is observed for all three phases. We also find that for samples of constant Sr doping the effect of  $P(\text{O}_2)$  on magnetic transition temperature is significant. On cooling both rhombohedral and orthorhombic samples exhibit structural anomalies close to the magnetic ordering temperature. This anomaly exhibited by the orthorhombic phase will be briefly discussed. This work was supported by the NSF Office of Science and Technology Centers under contract DMR 91-2000.

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**MS10.06.05 THE TRANSITION FROM POLARONIC TO ITINERANT ELECTRONS IN THE ORTHOMANGANITES.** John B. Goodenough and J.-S. Zhou, Center for Materials Science & Engineering, ETC 9.102 University of Texas at Austin, Austin, TX 78712-1063

The  $\text{AMO}_3$  perovskites containing transition-metal atoms have an  $\text{MO}_3$  array with M-O-M bond angles  $180^\circ - \phi$  in which the angle  $\phi$  increases with the mismatch of the A-O and M-O equilibrium bond lengths. The tight-binding bandwidths for the  $\pi$ -bonding  $t$  and  $\sigma$ -bonding  $e$  orbitals of d-orbital parentage are  $w_\pi < w_\sigma$ . In the orthomanganites  $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$  with A an alkaline earth, the octahedral site high-spin  $\text{Mn}^{3+}$  ions have a d-electron configuration  $t^3e^1:5E_g$  that is orbitally twofold degenerate, and the on-site electron-electron coulomb energy for adding a fifth d electron is  $U_\sigma = W_\sigma > W_\pi$ . Consequently the equilibrium reaction  $t^3e^1 = t^3\sigma^*1$  for a first-order transition from localized- $e$  to itinerant- $\sigma^*$  electrons is shifted to the right as the spin-dependent integral  $t_{ij} = e_\sigma \lambda_\sigma^2 \cos\phi \cos(\theta_{ij}/2)$  is increased by decreasing  $\phi$ , by increasing  $\lambda_\sigma$  with hydrostatic pressure, or by reducing the angle  $\theta_{ij}$  between spins on neighboring Mn atoms with an external magnetic field. The evolution from polaronic behavior ( $t_{ij} < \hbar\nu_R$ ) to narrow-band behavior ( $t_{ij} > \hbar\nu_R$ ) is shown to pass through a novel vibronic state in which the electrons of  $e$ -orbital parentage are strongly coupled to a cooperative, dynamic Jahn-Teller deformation mode of frequency  $\nu_R$ . A first-order vibronic-polaronic transition occurs at a Curie temperature  $T_C$ . The "colossal" negative magnetoresistance is associated with an increase in  $T_C$  with magnetic field, but a giant magnetoresistance below  $T_C$  occurs where an applied magnetic field either transfers Anderson localized holes to the dispersionless vibronic band or, at  $x \approx 0.5$ , shifts a first-order transition from a charge-ordered, antiferromagnetic phase to a ferromagnetic, metallic phase.

**PS10.06.06 STRUCTURE AND GIANT MAGNETORESISTANCE OF  $\text{La}_{1/3}\text{R}_{1/3}\text{Ca}_{1/3}\text{MnO}_3$ ;** by Guanghui Rao, Jingkui Liang, Jirong Sun and Yezhou Sun; Institute of Physics, Chinese Academy of Sciences, Beijing 100080, P.R. China

The crystal structure of  $\text{La}_{1/3}\text{R}_{1/3}\text{Ca}_{1/3}\text{MnO}_3$  was refined by conventional Rietveld method with x-ray powder diffraction data. The structure belongs to an orthorhombically distorted perovskite-type, S.G.  $Pnma$ . Under our synthesis conditions (sintering the mixture of  $\text{R}_2\text{O}_3$ ,  $\text{CaCO}_3$  and  $\text{MnO}_2$  at 1373K for 96hr with two intermediate grindings), single-phase samples with the orthorhombic structure were obtained for  $R=\text{La, Pr, Nd, Sm, Eu, Ga}$  and  $\text{Tb}$ ), while the samples with  $R=\text{Dy, Er, Tm}$  and  $\text{Y}$  consist of the orthorhombic phase (S.G.  $Pnma$ ) and a hexagonal phase (S.G.  $P6_3cm$ ). The stability of the orthorhombic structure seems to be determined by a geometrical tolerance criterion for the perovskite:  $t \approx 0.945$ . The magnetoresistance in a field up to 1T and the magnetization as well as  $ac$  susceptibility of the samples were measured. A negative giant magnetoresistance effect as high as -96% was observed in bulk  $\text{La}_{1/3}\text{Nd}_{1/3}\text{Ca}_{1/3}\text{MnO}_3$  at a field of 0.67T. An insulator-metal transition occurs far below Curie temperature. The conductivity of the compounds exhibits a metallic behavior at low temperature, and a semiconductor behavior at high temperature dominated by magnetic polaron hopping. The correlation between the distortion of perovskite structure, magnetic structure and magnetoresistance was investigated.