Orbital and magnetic order in $LaMn_{1-x}Cr_xO_{3+\delta}$ (x=0.0-0.25) compounds

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The effect of Cr substitution for Mn on the orbital order-disorder (Jahn-Teller) transition, prototypically exhibited by stochiometric $LaMnO_3$ at 750 K, remained unexplored to present times. Recent work (1, 2) on $LaMn_{1-x}Cr_xO_{3+\delta}$ compounds mainly focused on their magnetic/structural properties addressing questions like the nature of the magnetic Mn^{3+}-Cr^{3+} (double exchange (DE) or super exchange(SE)) which is responsible for the FM behaviour observed upon increasing x in hole-free specimen. In the present work Cr doping at Mn site was employed to investigate its influence on the J-T distortion. Cr^{3+}, with an ionic radius (0.615 Å) comparable to that of high-spin Mn^{3+} (0.64Å) should not cause extensive lattice distortion. However, Cr^{3+}, being isoelectronic to Mn^{4+} should introduce non-distorted $Cr^{3+}O_6$ octahedra, randomly distributed at spatially fixed Mn^{3+} sites.

The $LaMn_{1-x}Cr_xO_{3+\delta}$ samples ($0.00 \leq x \leq 0.25$) were investigated by electrical resistivity, ρ(T), differential thermal analysis, DTA, (300-1100K) and χ_{ac} measurements (80-300 K). The powders of the compounds have been prepared using high purity La_2O_3, $Cr(NO3)_3 9H_2O$ and MnO_2 by solid state reaction and were exposed finally to T=1300°C in air. Pressed samples of different Cr content were simultaneously subjected to heat treatments–densification at T=900-1300°C, under controlled atmospheres (P_{O2}=210-10^{-6} mbar), to obtain specimen with successively lower O_2-excess up to $\delta \approx 0$.

The results of the ρ(T) measurements show semiconducting behaviour. For specimen with δ<0.04 a step like decrease of the ρ(T), observed at 600-750K, is recognized as the signature of the J-T transition. In Fig.1 the transition temperatures, T_{J-T}, obtained for specimen with $\delta \approx 0$, are plotted against Cr doping, x. They show an approximately linear decrease of T_{J-T} upon increasing x. The DTA investigations show a single peak for each one of the $LaMn_{1-x}Cr_xO_3$ ($\delta \approx 0$) specimen, obviously reflecting the exchange of latent heat at the J –T transition. The peak temperatures are found very close to the corresponding T_{J-T}, values. The DTA peaks progressively broaden, while the latent heat (area under peak) shows a strong reduction upon increasing x, approaching zero for samples with x≥0.15. It is therefore clear that both ρ(T) and DTA results unambiguously demonstrate that Cr^{3+} strongly affects the orbitally ordered state. The displacement of T_{J-T} might be attributed to a suppression of the cooperative J –T distortion caused by the reduction of the concentration of Mn^{3+} and possibly by an additional reduction of local J-T distortion of $Mn^{3+}O^2{}_6$ neighboring with non distorted $Cr^{3+}O^{2-}{}_6$. It should however be remarked that the data of Fig.1 are in contrast to conclusions drawn in ref. (3). Furthermore, as shown in Fig.1, Cr^{3+} clearly causes a significantly stronger displacement of T_{J-T} than the isoelectronic nonmagnetic Ga^{3+} despite their size similarity (r_{Ga3+}=0.62 Å).

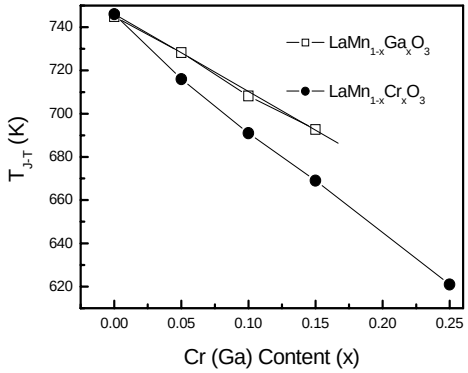

Fig.1: Displacement of the Jahn Teller transition by B=Cr^{3+}, Ga^{3+} in $LaMn_{1-x}B_xO_3$ compounds.

The results of the χ_{ac} measurements for O_2-rich specimen ($\delta \geq 0.09$) show DE-dominated FM transitions, with non-monotonic variation of the Curie temperatures with Cr doping, in accordance with literature data(4). For specimen with low Mn^{4+} content, δ<0.04, transitions to the CA-AFM have been observed at T_{CA} <140K. The spontaneous susceptibility exhibits a steep increase suggesting a considerable enhancement of the FM interactions in specimen with x≥0.15. On the other hand, T_{CA} shows a minimum at x=0.10-0.15. As the position of the minimum apparently depends on the Mn^{4+} content it rather indicates a competition of magnetic DE and SE interactions. The enhancement of FM interactions resulting in a strengthening of the CA-AFM state seems therefore to be favored in Mn^{4+} -free specimen.

References:

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