Impact of charge doping, oxygen disorder and hydrostatic pressure on thermoelectric and magnetic properties of $NdBa_{0.94}La_{0.06}Co_2O_{5+\delta}$

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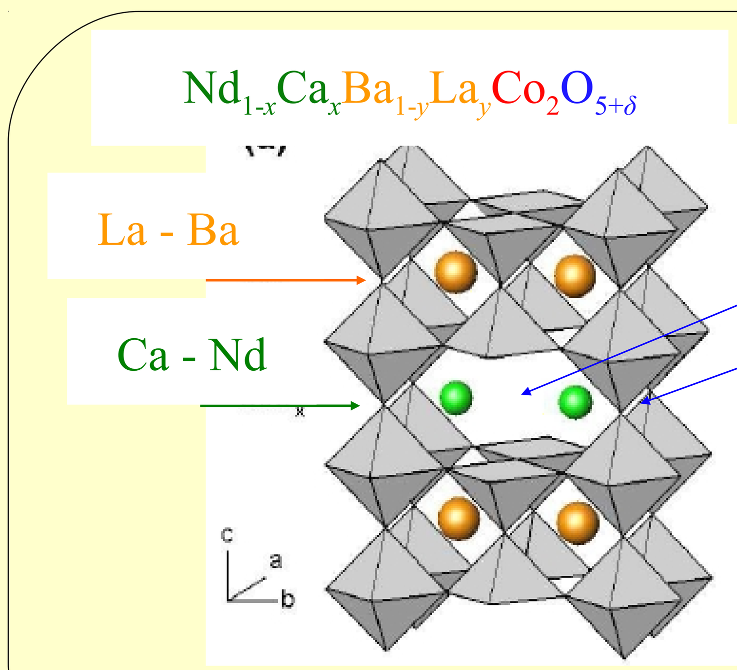
- The layered perovskite $NdBaCo_2O_{5.5}$ is characterized by a sequence of magnetic and electronic phase trainsitions observed with increasing temperature: antiferromagnet-ferromagnet (T_N=240 K), ferromagnet-paramagnet (T_C=260 K), and insulator-metal (T_{MIT}=350 K).
- The substitution of Ca for Nd (hole doping) have caused a decrease of T_N down to zero for 10% of Ca, and increase of T_C up to coincidation with T_{MIT} for 16% of Ca.
- The critical temperatures of above mentioned phase transitions can be modified by a substitution at the Ba- or Co-site or by a change of oxygen content δ.
- We have studied the compounds with a wide range of the effective charge doping to probe separately the effects of disruption of the oxygen vacancy ordering and the charge doping.
- Investigation of the thermoelectric and magnetic properties permitted separation of the charge doping and oxygen disorder effects [1,2].
- The magnetic properties under hydrostatic pressure were investigated as well, in order to make a comparison of changes of T_N, T_C, and T_{MIT} between the cation hole-doped $Nd_{0.94}Ca_{0.06}BaCo_2O_{5+\delta}$ [1] and electron-doped $NdBa_{0.94}La_{0.06}Co_2O_{5+\delta}$ systems.

Experimental set-up

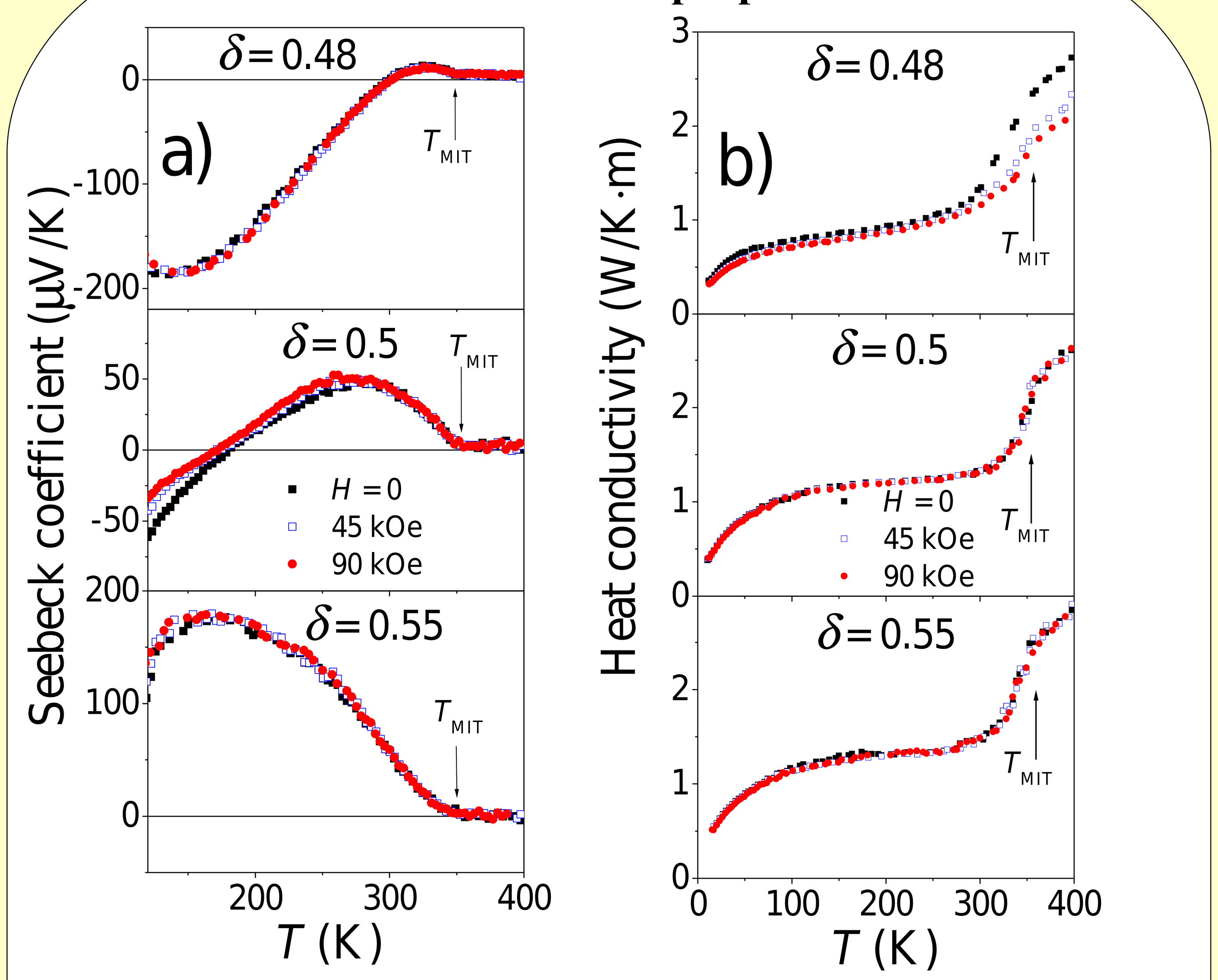
The EasyLab MCell10 dedicated for SQUID magnetometer.

Crystal structure



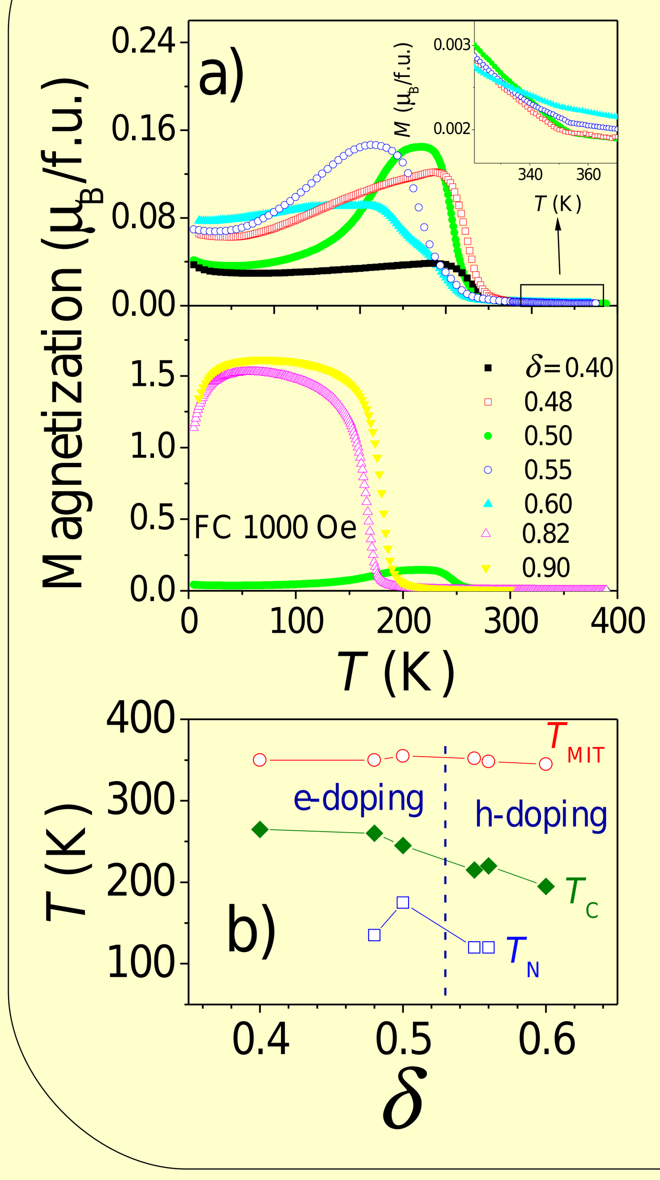
Layers aligned along the *c*-axis:
… - BaO – CoO_2 – RO_δ – CoO_2 – …

Thermoelectric properties



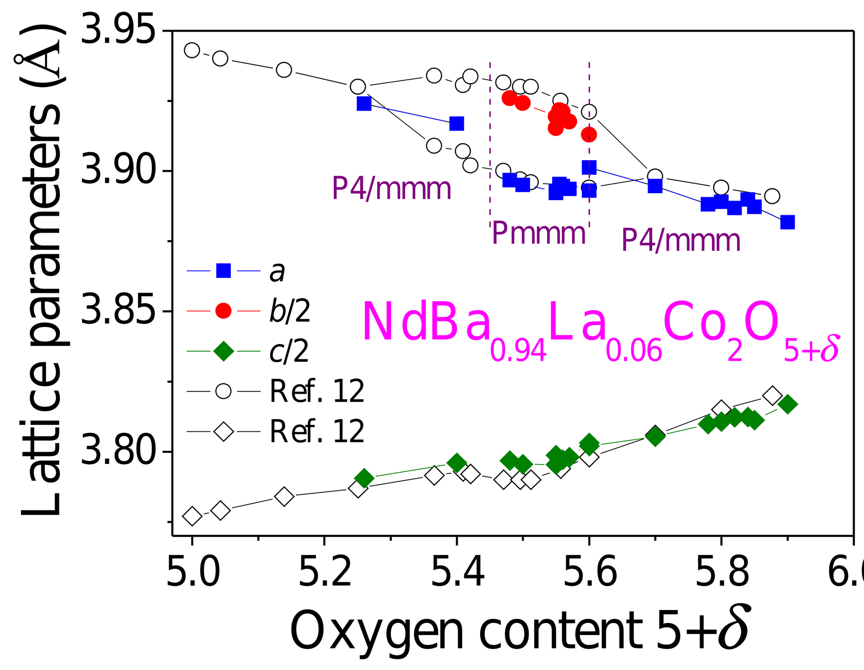
- The thermoelectric properties were investigated for oxygen contents, for which the oxygen vacancy ordering of orthorhombic phase was maintained.
- Within this range of oxygen content the thermoelectric properties are very similar to those of the pure system $GdBaCo_2O_{5+\delta}$ [4].
- A clear relationship between Seebeck coeff. and the charge doping (and proper charge carrier type) for $NdBa_{0.94}La_{0.06}Co_2O_{5+\delta}$ is observed (Fig. a). particulary for *T*=150-200 K.
- For *T*=200–300 K both electrons and holes give the contribution to charge transport, with holes having considerably higher mobility [2].
- The temperature dependence of thermal conductivity (Fig. b) exhibits the decrease at the T_{MIT} due to removal of the electronic contribution for the insulating phase as observed for $Nd_{1-x}Ca_xBaCo_2O_{5.5}$ [1].

Magnetic properties vs. Oxygen content



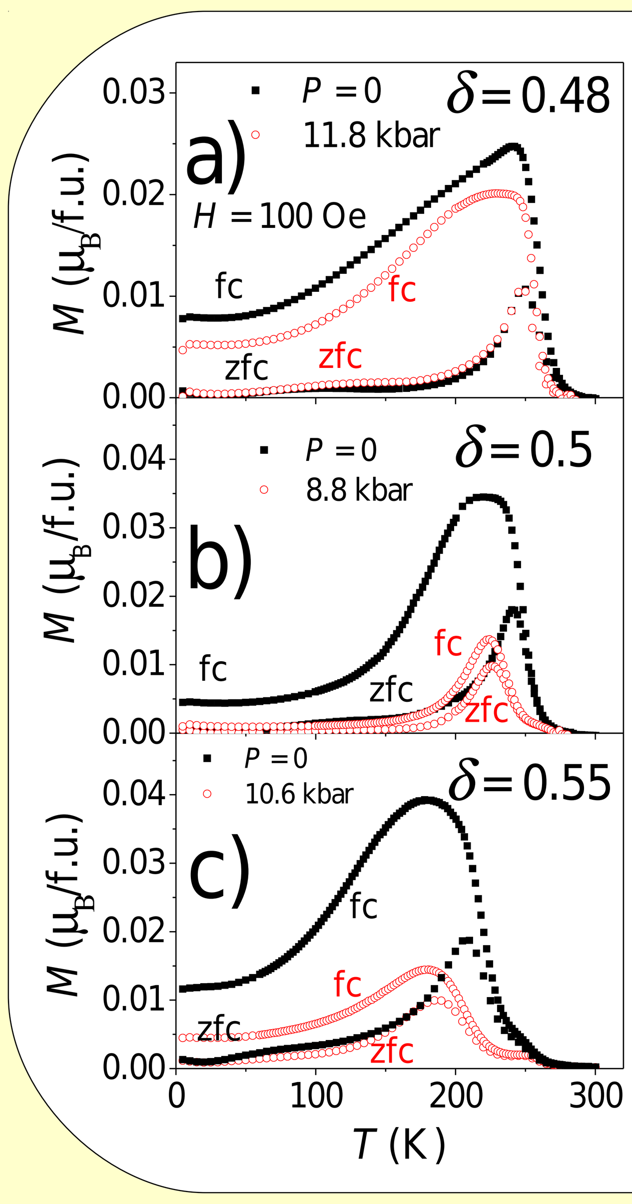
- T_N i T_{MIT} have maximal values for δ=0.5
- Charge doping by the change of oxygen content leads to a decrease of T_N with simultaneous suppression of the size of the AFM phase fraction. An AFM phase is not present for δ = 0.4 or δ = 0.6.
- Maximum of T_C is neither observed at the optimum oxygen ordering content δ = 0.5 nor at the optimum charge doping (δ = 0.53)

Structural parameters vs. Oxygen content

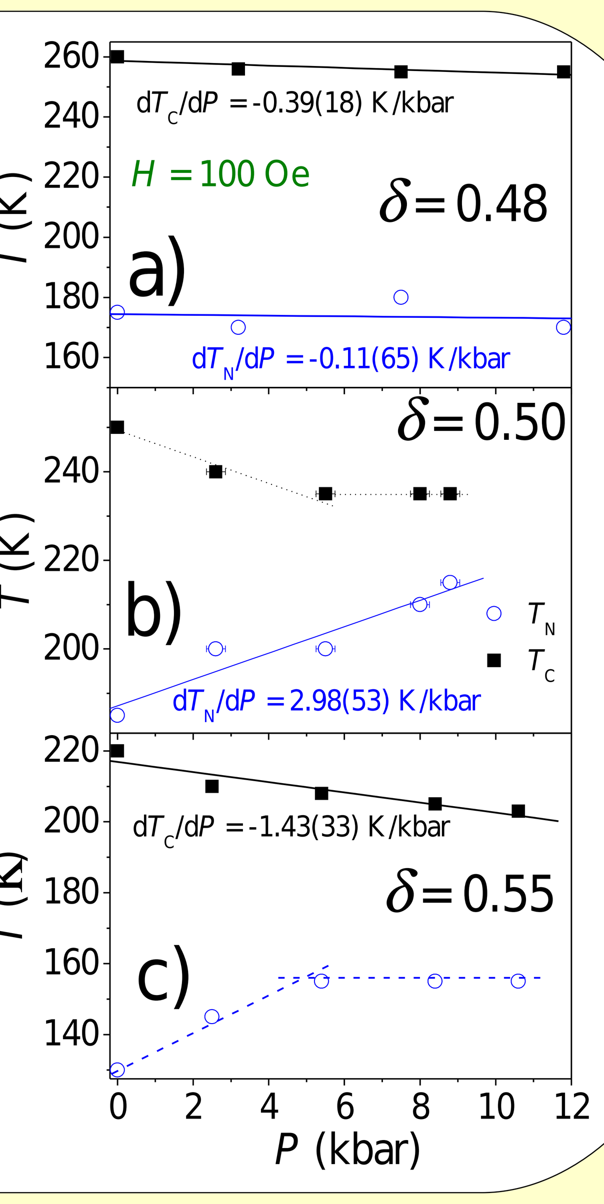


- For δ = 0.4–0.6, the crystal structure is orthorhombic with oxygen vacancy ordering.
- The samples on the boundary between the orthorhombic and tetragonal phase ranges (e.g., δ=0.6), can be refined as any of the two phases with similar quality. This indicates possible coexistence of both phases in the transitional range of oxygen contents.

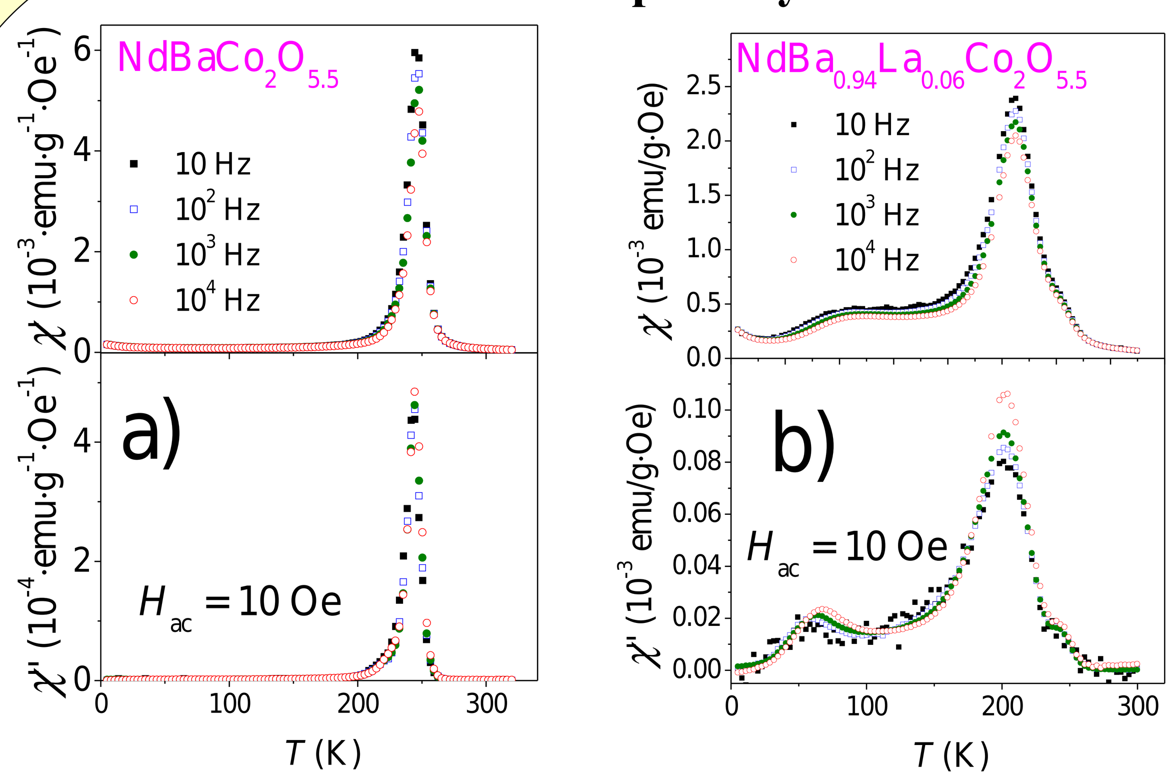
T_C and T_N vs. pressure



- For $NdBaCo_2O_{5.5}$ [4]:
dT_N/dP = 1.03 K/kbar, dT_C/dP=0.62 K
- The La-Ba substitution (slight e-doping) significantly enhances the pressure coefficient of T_N.
- The magnetic transition at T_N is likely to be of the first order.
- These results suggest that the hydrostatic pressure stabilizes the antiferromagnetic phase and the stabilization is enhanced not only for the hole doped compositions [4] but also for electron doped ones.
- The stabilization of AFM phase under pressure is enhanced after hole doping by oxygen defects for $NdBa_{0.94}La_{0.06}Co_2O_{5.55}$ (Fig. c), but it is suppressed for considerably electron doped $NdBa_{0.94}La_{0.06}Co_2O_{5.48}$ (Fig. a).

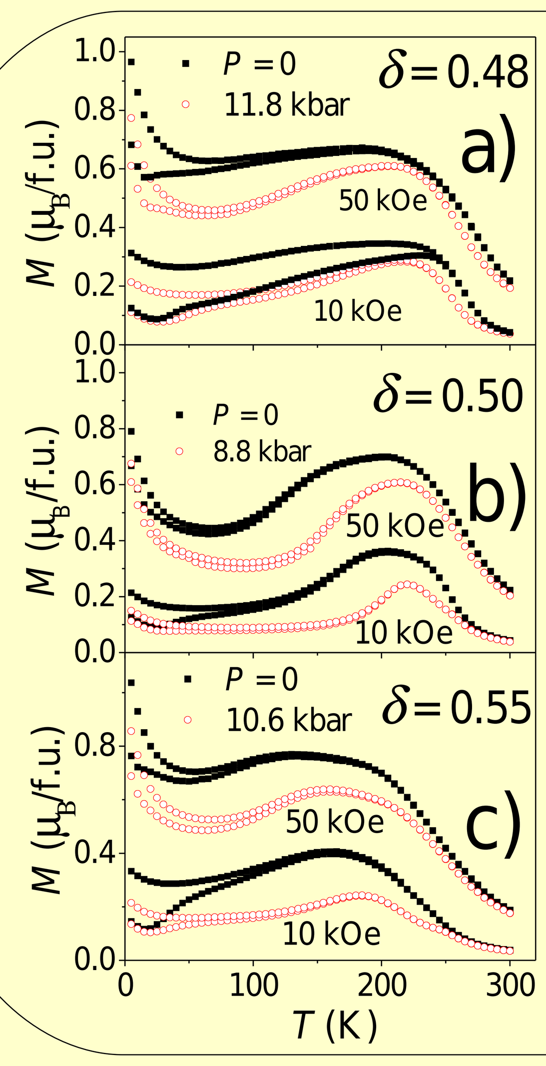


AC susceptibility



- Sharp maximum at T_C is observed for pure $NdBaCo_2O_{5.5}$.
- The La–Ba substitution results in a shift of the high-temperature peak, observed at T_C for $NdBaCo_2O_{5.5}$, to lower *T*'s, confirming decrease of T_C by La^{3+} substitution.
- Second rather broad peak is observed below T_N for La - substituted (70–80 K), which may be connected to the ferrimagnetic contribution in antiferromagnetic matrix, seen in dc magnetic measurements.

The magnetic properties in high magnetic fields



- A clear divergence between M_{ZFC} and M_{FC}, starting from T_N down to *T*=5K, exists even in the magnetic field of 50 kOe.
- This divergence was observed in $Nd_{1-x}Ca_xBaCo_2O_{5.5}$ system [4] and was explained by appearance of the field-induced metastable fraction of ferrimagnetic phase [4].
- For *H*=50 kOe, significant increase in magnetization at low *T*'s (5–25 K), was explained as the magnetic polarization of the Nd sublattice [4].
- In Ref. 5, it was shown that the strength of exchange interactions between the lanthanide ions and the AFM-ordered Co sublattice can be described with the parameter B_{ex} = 11.0(5) kOe, within molecular field theory.
- For *H*=10 kOe, which is of the order of B_{ex}, the *M*(*T*) dependences do not reveal any significant increase at low temperatures.

- **The single-phase orthorhombic samples with oxygen orderring were observed for 0.45 < δ < 0.55.**
- **We have found clear relationship between doping with cation and oxygen and the Seebeck coefficient in $NdBa_{1-y}La_yCo_2O_{5+\delta}$ (y=0-0.06, δ=0.48; 0.5; 0.55).**
- **Thermal conductivity exhibits characteristic decrease at T_{MIT} due to removal of the electronic contribution and is well correlated with suppression of the Seebeck coefficient.**
- **The T_{MIT} and T_N reach maximum values for slightly electron doped sample with a perfect oxygen ordering δ = 0.5 while the T_C shows continuous decrease with the increase of δ.**
- **The hydrostatic pressure was observed to stabilize the antiferromagnetic phase for $NdBa_{0.94}La_{0.06}BaCo_2O_{5.5}$, whereas the electron doping of $NdBa_{0.94}La_{0.06}Co_2O_{5.48}$ was found to suppress this stabilization.**

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