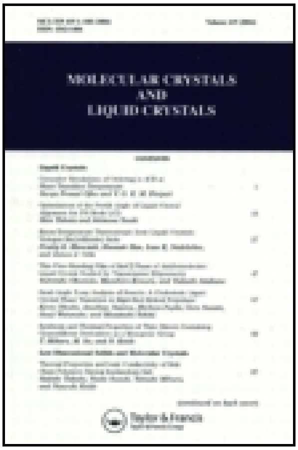

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# EFFECT OF COBALT SUBSTITUTION ON THE JAHN-TELLER DISTORTION OF THE $NaNiO_2$ LAYERED OXIDE

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## ABSTRACT

$NaNiO_2$ exhibits a layered structure made of $NiO_2$ slabs between which $Na^+$ ions are inserted in octahedral environment. Trivalent nickel ions in the low spin state ($t_2^6e^1$) exhibits a Jahn-Teller effect which leads to a distortion of the $NiO_6$ octahedra and hence to a macroscopic lattice distortion. The partial substitution of trivalent cobalt for nickel ($NaNi_{1-y}Co_yO_2$) allows to suppress the structural distortion for $y \geq 0.22$. This behavior results from the competition between the stabilization of $Ni^{3+}$ ions in distorted environment and the strong stabilization of the isotropic $Co^{3+}$ ions in octahedral environment.

## INTRODUCTION

The $NiO_2$ slab made of edge-sharing $NiO_6$ octahedra is the main structural part of nickel hydroxide ($Ni(OH)_2$) and lithium nickelate ($LiNiO_2$), which are both involved as positive electrode material of secondary batteries (1). The former material has been used for almost one century in alkaline batteries like Nickel//Cadmium and, more recently, in Nickel//Metal Hydride ones. The two types of cells are nowadays the most widely used systems for high specific energy and reliable electrochemical generators. Concerning the future, lithium nickelate is one of the most promising material, since, in lithium batteries, the intercalation process is very well reversible (2-4) ; moreover, this material leads to a high cell voltage, ranging between 3.6 and 4.2 V, which allows to use carbon as negative electrode in order to improve the cell life (5).

In all systems, trivalent nickel plays an important role; it appears as the reduced state in the $Li_xNiO_2$ system, as the oxidized one in the $\beta$(II)-$Ni(OH)_2$/$\beta$(III)-NiOOH system and as an intermediate state in the $\alpha$-$Ni(OH)_2$/$\gamma$-NiOOH system. In all materials, magnetic studies have shown that the trivalent nickel ions are in the low spin state ($t_2^6e^1$). During redox reaction $Ni^{II}$ ($t_2^6e^2$) or $Ni^{IV}$ ($t_2^6e^0$) appears in the reduced and oxidized phases respectively. As a result of the strong stabilization of the $e^1$ level by a Jahn-Teller effect, a distortion of $NiO_6$ octahedra is expected in the $Ni^{III}$ containing compounds. In fact, macroscopic distortion of the structure has not been reported in any of these systems. However, important broadening of the X-ray diffraction lines for stoechiometries close to NiOOH or in some cases to $LiNiO_2$, suggest that local distortion may occur (6). In the case of the homologous sodium nickelate ($NaNiO_2$) a strong macroscopic structural distortion does take place (7-9) ; in this material, the presence of large size alkali ion may decrease the interslab bonding and therefore facilitate the distortion of each individual slab.

In order to simulate the effect on the $Ni^{III}$ Jahn-Teller distortion of the presence of an isotropic ion like $Ni^{2+}$ or $Ni^{IV}$ in $Li_xNiO_2$ or $H_xNiO_2$ systems, a general study of the effect of the substitution of trivalent cobalt $(t_2{}^6e^0)$ for nickel in $NaNiO_2$ has been undertaken. These materials, with general formula $NaNi_{1-y}Co_yO_2$, have been previously obtained in our lab as they are used as precursor in the preparation of well crystallized oxyhydroxides and hydroxides (10,11).

## RESULTS AND DISCUSSION

### *Crystal chemistry and X-ray diffraction study*

The cobalt substituted sodium nickelates were obtained by direct synthesis from the oxides ($Na_2O$, NiO, $Co_3O_4$) in a gold boat. Several thermal treatments (15 h at 600°C, 20 h at 800°C and 48 h at 800°C) under an oxygen stream are necessary to get pure materials.

The X-ray diffraction patterns ($Co_{K\alpha}$) were obtained with an INEL CPS 120 curve position sensitive detector.

As previously reported (10), the $NaNi_{1-y}Co_yO_2$ solid solution can be obtained only for y ranging from 0 to 0.5 ; for higher values of y, a mixture of the limit composition $NaNi_{0.5}Co_{0.5}O_2$ with $NaCoO_2$ is obtained, whatever the experimental conditions.

In the composition domain $0 \leq y < 0.2$ the materials crystallize with a monoclinic symmetry like for the $NaNiO_2$ parent phase, while for higher cobalt amounts the monoclinic distortion of the $\alpha$-$NaFeO_2$ type structure disappears, leading to the rhombohedral symmetry of $NaCoO_2$. In order to discuss the structural modifications, it is useful to compare, as reported in Fig. 1, the variations vs y of the intersheet and M-M intrasheet distances. In that range, for all studied compositions, the existence of two in-plane M-M distances emphasizes the presence of the monoclinic distortion; the value of the $a_{mon.}/b_{mon.}$ ratio characterizes the intensity of the distortion. It decreases continously when y increases up to y = 0.2. For this value, the ratio of the two in-plane distances becomes equal to $\sqrt{3}$ which is the ideal value for a triangular lattice.

For the highest cobalt amounts ($0.2 \leq y \leq 0.5$), the small decrease vs y of the M-M intrasheet distance ($a_{hex.}$) reflects the difference in ionic radius between trivalent nickel and cobalt ions. As shown in Fig. 1, the $NaNi_{0.5}Co_{0.5}O_2$ and $NaCoO_2$ phases exhibit very close unit cell parameters. It results that the non-existence of a solid solution between these two compositions is not understood. As it cannot result from steric constraints, one can assume that there is an electronic contribution, resulting from the distribution of the paramagnetic $d^7$ nickel ions and the diamagnetic $d^6$ cobalt ones, that destabilises the $0.5 < y < 1$ compositions vs the $NaNi_{0.5}Co_{0.5}O_2$ and $NaCoO_2$ ones.

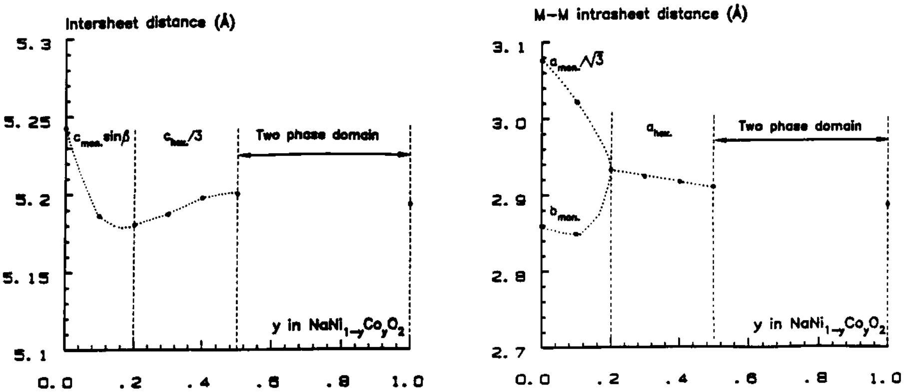


FIGURE 1 Variation of the unit cell parameters vs y in the $NaNi_{1-y}Co_yO_2$ system

### *Thermal study*

As it is well known that the Jahn-Teller distortion is very sensitive to temperature, a systematic thermal study has been realized by differential scanning calorimetry and X-ray diffraction. The shape of the thermal curves obtained for $NaNiO_2$ and $NaNi_{0.9}Co_{0.1}O_2$, reported in Fig. 2, illustrates the reversibility of the transition. The substitution of cobalt for nickel decreases simultaneously the transition temperature and the energy involved by the monoclinic → rhombohedral structural modification (Table I). For the $NaNi_{0.8}Co_{0.2}O_2$ composition the monoclinic variety appears only on cooling below RT, while for cobalt amounts larger than 0.22 no monoclinic distortion is observed whatever the temperature. The variation vs cobalt amount of the transition enthalpy indicates that it becomes close to 0 for $y = 0.22$. This behavior, which shows that the monoclinic variety is the most stable at low temperature only for $y < 0.22$, results from the competition between the stabilizing energy due to the Jahn-Teller effect on trivalent nickel and the energy lost to distort the $CoO_6$ octahedra around the isotropic $Co^{III}$(LS) ion. The reversibility of the structural transition is also well emphasized by the X-ray diffraction study. As an exemple, for the $NaNi_{0.9}Co_{0.1}O_2$ composition at 350 K only the monoclinic variety is detected on the diffraction pattern, the rhombohedral one appears at 375 K and there is no trace of the monoclinic one at 400 K.

### *Magnetic characterization*

The magnetic study has been realized with a MANICS (DSM5) susceptometer. The variation of the reciprocal susceptibility vs temperature is reported in Fig. 3 for $NaNiO_2$ and $NaNi_{0.9}Co_{0.1}O_2$. In both cases, the structural transition is characterized by a break on the curve without modification of the slope. This result indicates that there is no modification of the spin configuration at the phase transition. The value of the experimental Curie constants (0.49 ($y = 0$) and 0.41 ($y = 0.1$)) agree with the presence of low spin trivalent nickel and cobalt in these materials ($C_{theor.} = 0.38$ and 0.34 for $y = 0$ and $y = 0.1$ respectively). Upon decreasing temperature, only a small hysteresis effect is observed. The extrapolation at room temperature of these susceptibility curves shows that the $\theta_p$ paramagnetic Curie temperatures are positive as a result of the predominating ferromagnetic e-$p_\sigma$-$p_\sigma$-e coupling. The existence of ferromagnetic interactions within the slab leads to the metamagnetic character previously reported by Bongers et al. from a single crystal study (8).

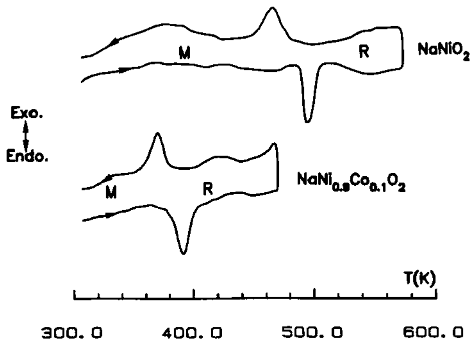


FIGURE 2 Differential thermal analysis of the $NaNiO_2$ and $NaNi_{0.9}Co_{0.1}O_2$ oxides

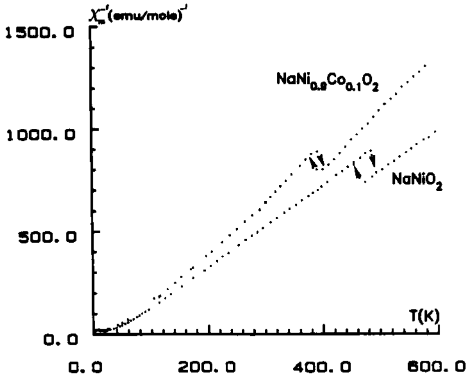


FIGURE 3 Variation of the magnetic susceptibility vs temperature of the $NaNiO_2$ and $NaNi_{0.9}Co_{0.1}O_2$ oxides.

TABLE I - Thermal parameters of the monoclinic → rhombohedral transition in the $NaNi_{1-y}Co_yO_2$ phases. T1 temperature of the beginning of the transition. T2 temperature of the end of the transition.

| y | Symmetry at RT | $T_1$ (K) | $T_2$ (K) | -ΔH (kcal/mole) |
|---|---|---|---|---|
| 0 | monoclinic | 490 | 510 | 0.95 |
| 0.10 | monoclinic | 370 | 405 | 0.54 |
| 0.20 | rhombohedral | 275 | 300 | 0.13 |
| $0.22<y<0.5$ | rhombohedral | <77 (?) | - | - |

***Electric properties***

The electrical conductivity data have been obtained with the four probes method with a home-made system. The pellets of the materials have been sintered at 800°C, their compactness is close to 0.85. The variations of the logarithm of the conductivity vs reciprocal temperature are plotted in Fig. 4 for increasing cobalt amounts. For materials with monoclinic symmetry, the variation of the conductivity is characteristic of a semiconductor behavior with an activation energy ranging from 0.29 to 0.23 eV. At the transition temperature a break is observed in all cases in the conductivity curves, while a decrease of the activation energy is observed at higher temperature. The electrons remain however localized in the explored temperature range (4-650 K). An electronic delocalisation at temperature higher than 650 K has been previously reported

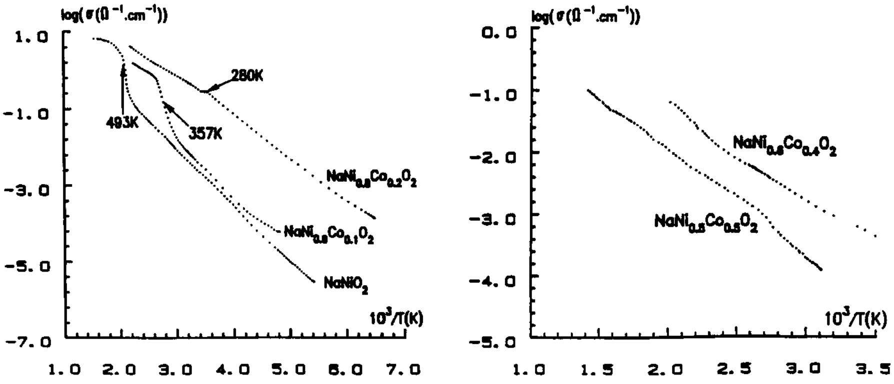
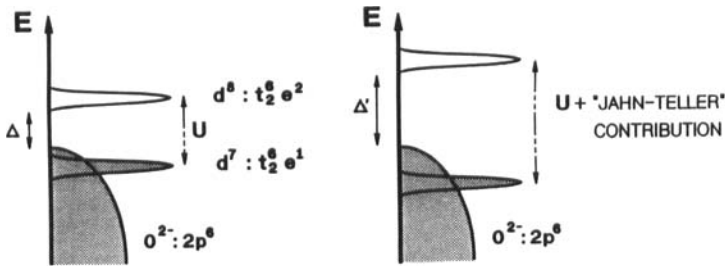


FIGURE 4 Variation of the electric conductivity vs temperature of $NaNi_{1-y}Co_yO_2$ phases.

by Molenda et al. for $NaNiO_2$ (12). Nevertheless, surprisingly, these authors do not found any evidence of discontinuity on the conductivity curve at the transition temperature. It should be noticed that the conductivity increases with the cobalt amount for $0 \leq y < 0.2$ while it decreases for $y > 0.2$.

In $NaNiO_2$, as a result of edge-sharing of the distorted $NiO_6$ octahedra and of low spin state of $Ni^{3+}$ ions, the electronic transfer can only occurs through the $Ni/^{O}\backslash Ni$ overlap via the e orbitals. Moreover, this overlap is very sensitive to the $Ni/^{O}\backslash Ni$ bond angle which is strongly modified by the Jahn-Teller distortion. In order to explain the electronic behavior of these materials in the vicinity of the transition temperature, the energy diagram shown in Fig. 5 is proposed. The strong electronic localisation allows to use an ionic model with the successive redox couples $Ni^{3+}/Ni^{2+}(d^8 : t_2^6e^2)$ and $Ni^{4+}/Ni^{3+}(d^7 : t_2^6e^1)$ separated by the intra-atomic interaction energy U. According to J. B. Goodenough, in these very oxidized materials



HIGH TEMPERATURE
($E_a \sim \Delta$)
RHOMBOHEDRAL SYSTEM

LOW TEMPERATURE
($E_a \sim \Delta'$)
MONOCLINIC SYSTEM

FIGURE 5 Schematic energy diagram of $NaNiO_2$.

the $O^{2-}$ oxygen level would be situated slightly higher than the $Ni^{4+}/Ni^{3+}$ redox couple (13, 14). The activation energy $E_a$ would thus correspond to the energy difference between the top of the oxygen level and the first $Ni^{3+}/Ni^{2+}$ unoccupied level. In the distorted state, the increasing splitting which results from the Jahn-Teller effect leads to an increase of the activation energy as experimentally observed. The variation with the cobalt substitution of the conductivity results from the competition between the decrease in $Ni^{3+}$ ion concentration and the tendency for the $\mathrm{Ni} / ^{\mathrm{O}} \backslash \mathrm{Ni}$ bond angle to become closer to 90°.

## CONCLUSION

In conclusion, the partial substitution of cobalt for nickel in sodium nickelate allows to suppress the cooperative Jahn-Teller distortion. Nevertheless, for small cobalt amounts ($y < 0.22$), according to the temperature, both varieties are observed. The structural transition has a strong influence on the electronic properties although the low spin configuration is maintained for all compositions and whatever the temperature.

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## REFERENCES

1. C. Delmas, Proceedings of the MRS "Solid State Ionics" Meeting, Boston (1992) (in press).
2. M.G.S.R. Thomas, W.I.F. David and J.B. Goodenough, Mat. Res. Bull., 20, 1137 (1985).
3. C. Delmas and I. Saadoune, Solid State Ionics, 53-56, 370 (1992).
4. M. Broussely, F. Perton, J. Labat, R.J. Staniewicz and A. Romero, J. Power Sources (in press).
5. J.R. Dahn, U. Van Sacken, M.W. Juzkow and H.A.P. Janaby, J. Electrochem. Soc., 138 (8), 2207 (1991)
6. A. Rougier, L. Gautier and C. Delmas, Private communication.
7. L.D. Dyer, B.S. Borie and G.P. Smith, J. Amer. Chem. Soc., 76, 1499 (1954).
8. P.F. Bongers et U. Enz, J. Solid State Commun., 4, 153 (1966).
9. J.J. Braconnier, C. Delmas and P. Hagenmuller, Mat. Res. Bull., 17, 993 (1982).
10. C. Delmas, Y. Borthomieu, C. Faure, A. Delahaye and M. Figlarz, Solid State Ionics, 32/33, 104 (1989).
11. C. Delmas, C. Faure and Y. Borthomieu, J. Mat. Sc. and Eng., B13, 89 (1992).
12. J. Molenda and A. Stoklosa, Solid State Ionics, 38, 1 (1990).
13. J.B. Goodenough, private communication.
14. G. Dutta, A. Manthiram, J.C. Grenier and J.B. Goodenough, J. Solid State Chem., 96, 123 (1992).