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X-ray absorption spectroscopy studies of the off-center Ni^{2+} ions in $Ni_cMg_{1-c}O$ solid solutions

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ABSTRACT

In this work we present the x-ray absorption spectroscopy study of $Ni_cMg_{1-c}O$ ($0.01 \le c \le 1$) solid solutions. The extended x-ray absorption fine structure (EXAFS) above the Ni K-edge was analyzed using the multi-shell fitting procedure. It was found that nickel ions are located in a distorted environment and shift upon dilution to the off-center positions. This fact follows from two main results: (1) in the first shell, the average Ni–O distance increases linearly upon dilution; (2) in the second shell, the average Ni–Ni distance remains unchanged and decreases slightly at low nickel concentration while the dependence of the Ni–Mg distance has a break at $c \approx 0.6$ and is nearly constant below and above this concentration. The obtained results are discussed in comparison with the ones from x-ray diffraction, optical spectroscopies and magnetic measurements.

Keywords: $Ni_cMg_{1-c}O$, EXAFS, Ni K-edge, optical absorption, off-center position, solid solutions

1. INTRODUCTION

The $Ni_cMg_{1-c}O$ system forms a continuous series of solid solutions and at any composition has a rock-salt crystal structure in which metal ions occupy sites on a face-centered-cubic (fcc) lattice.[1,2] The lattice parameter *a* depends, according to the x-ray diffraction (XRD) data,[2] linearly on the composition: it increases slightly upon dilution from 4.1795 Å in pure NiO (c=1) to 4.2113 Å in pure MgO (c=0). In pure NiO, nickel ions are located at the centers of the octahedra formed by six oxygen atoms. However the question arises about their location upon dilution. It was observed previously by EPR, electro- and magneto-optical techniques[3,4] that in BaO doped with Mn^{2+} ions and in SrO doped with Cu^{2+}, Co^{2+}, Ni^{2+} and Ni^{+} ions, the transition metal ions are in off-center positions.

The crystal structure of $Ni_cMg_{1-c}O$ solid solutions is related to their magnetic properties. Since NiO is a type-II antiferromagnet with the Néel temperature T_N=523 K[5] and MgO is a diamagnet, the $Ni_cMg_{1-c}O$ system is ideal to study the effect of magnetic dilution on the magnetic properties. The nature of magnetic ordering in $Ni_cMg_{1-c}O$ depends on the relative signs and strengths of the nearest-neighbour (NN) and next-nearest-neighbour (NNN) superexchange interactions between two Ni^{2+} ions via oxygen ion.[6,7] The NN interactions, having ferromagnetic and antiferromagnetic character, occur within three atom chains Ni^{2+}-O^{2-}-Ni^{2+} with $\angle$NiONi = 90° (the so-called 90°-pairs) and are characterized by the exchange parameter J_{NN}. The NNN interactions, having antiferromagnetic character, occur within linear three atom chains Ni^{2+}-O^{2-}-Ni^{2+} with $\angle$NiONi = 180° (the so-called 180°-pairs) and are characterized by

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the exchange parameter J_{NNN}. Since the variation of the crystal lattice constant a in $Ni_cMg_{1-c}O$ is enough small (about 0.7%),[2] one can expect that upon dilution the corresponding changes in J_{NN} and J_{NNN} should be negligible. Therefore, one can take that the exchange parameters have the same values as in pure NiO: $J_{NN} \approx 34$ K and $J_{NNN} \approx 202$ K[7] (we use the positive and negative signs of J for antiferromagnetic and ferromagnetic interactions, respectively). A large difference between two values of the exchange parameters means that a very different magnetic behaviour can be expected (and is observed) upon dilution in $Ni_cMg_{1-c}O$.[1,2,8]

Among different structural methods the x-ray absorption spectroscopy (XAS) is a unique *direct* and *site selective* tool to study both electronic and atomic local environments around absorbing atom independently on presence or absence of the long-range order. It provides high resolution information on the short-range order compared to conventional direct structural methods, as x-ray, neutron and electron diffractions because the range of experimental data in the case of the K absorption edges extends above the absorption edge as long as up to the photoelectron wavevector value $k_{max} \approx 15\text{-}20$ Å^{-1} that would correspond to the maximum diffraction scattering vector $Q_{max} = 2k_{max} \approx 30\text{-}40$ Å^{-1} (the usual value of Q_{max} in diffraction experiments is equal to 20-30 Å^{-1}). Besides XAS can be applied to very diluted samples with concentrations of the probed element less than 1%. Thus XAS is very suitable technique to study the off-center problem.

In this work we report the XAS study of $Ni_cMg_{1-c}O$ ($0.01 \le c \le 1$) solid solutions on the Ni K-edge. The obtained structural information on the first and second coordination shells of nickel ions is presented and discussed in comparison with the results from other methods.

2. EXPERIMENTAL AND DATA ANALYSIS

The samples of $Ni_cMg_{1-c}O$ (c=0.10, 0.20, 0.35, 0.45, 0.50, 0.60, 0.70, 0.80, 0.90) were prepared using the procedure described in Refs. 1 and 2. Experimental x-ray absorption spectra at the Ni K-edge in $Ni_cMg_{1-c}O$ solid solutions and pure NiO (c=1) were measured in transmission mode at the ADONE storage ring (Frascati, Italy) on the PWA-BX2S wiggler beam line. The storage ring ADONE operated at the average energy 1.2 GeV and the maximum stored current 40 mA. A standard transmission scheme with a Si(220) channel-cut crystal monochromator and two ion chambers containing krypton gas was used. The experimental spectra were recorded at room temperature in the energy range from 8230 to 9300 eV. The samples were prepared from finely ground $Ni_cMg_{1-c}O$ powders and had a thickness leading to the absorption jump $\Delta\mu x$ about 0.6-1.8 depending on the composition.

The x-ray absorption spectra were treated using the "EDA" software package following the standard procedure.[9] The E_0 position, defining the zero wavevector (k=0), was set at the energy 8343 eV. This energy point was found by the alignment of the experimental and calculated EXAFS signals for pure NiO. The extracted experimental extended x-ray absorption fine structure (EXAFS) spectra $\chi(k)k^2$ and their Fourier transforms (FT) are shown in Fig. 1. The FT's were calculated in the range from 1.0 to 14.0 Å^{-1} with a Kaiser-Bessel window which gives results similar to the usual 10% Gaussian window but was found to be slightly more accurate.[9] Note that since FT's were calculated without phase correction, the positions of the peaks in Fig. 1(b) differ from their true crystallographic values. The EXAFS signals from the first two peaks were singled out by the Fourier filtering procedure in the range

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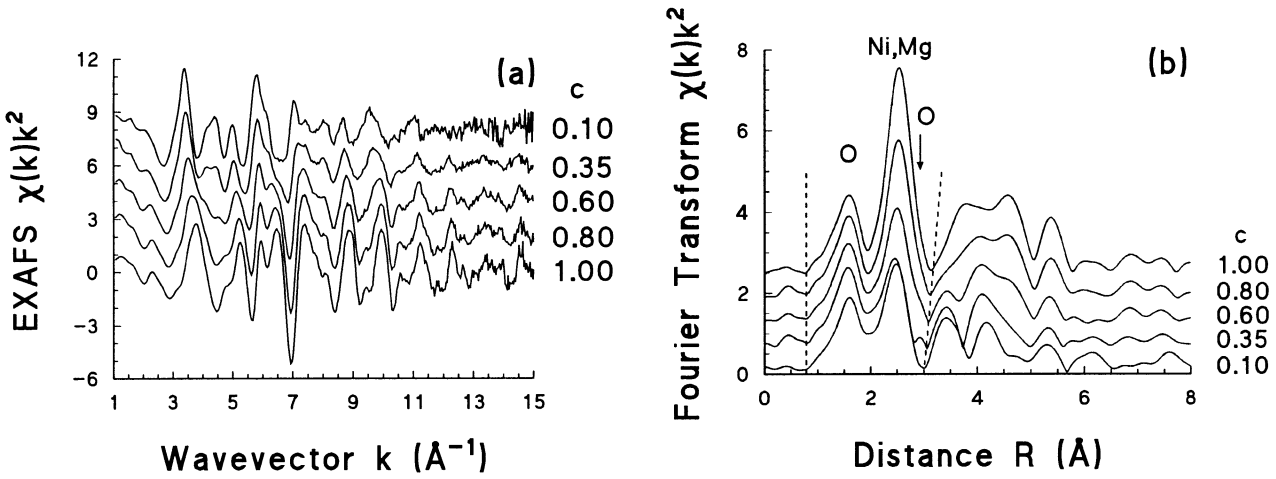

Fig. 1. Experimental EXAFS $\chi(k)k^2$ spectra in $Ni_cMg_{1-c}O$ (a) and their Fourier transforms (b). Dashed lines indicate the range used in the analysis.

shown in Fig. 1(b) by two dashed lines. These EXAFS signals were fitted using a multi-shell model

$$\chi(k) = \sum_{i=1}^{m} (N_i / kR_i^2) f_i(\pi, k) \exp(-2\sigma_i^2 k^2) \sin(2kR_i + \phi_i(\pi, k)).$$

Here $k = \left[(2m_e / \hbar^2)(E - E_0 - \Delta E_{0i})\right]^{1/2}$ is the photoelectron wavevector; ΔE_{0i} is the E_0 correction; N_i is the coordination number; R_i *is* the interatomic distance and σ_i^2 is the Debye-Waller (DW) factor describing both static and thermal disorder. $f_i(\pi,k)$ is the backscattering amplitude of the photoelectron, and $\phi_i(\pi,k)$ is the total phase shift function of the photoelectron due to the neighbour and absorber atoms. They were calculated using the FEFF3 code[10] for Ni–O_1 (R=2.095 Å), Ni–Ni_2 (R=2.965 Å), Ni–Mg_2 (R=2.965 Å) and Ni–O_3 (R=3.63 Å) pairs. The muffin-tin radii were chosen according to the Norman criterion and were reduced by a factor 0.85. They were equal to 1.14 Å for the absorber (Ni) and 0.94 Å (O), 1.16 Å (Ni) and 1.37 Å (Mg) for the neighbouring atoms. The complex Hedin-Lundqvist potential[11] was used to describe the exchange and correlation effects therefore $f_i(\pi,k)$ included automatically the correction on the mean free path of the photoelectron.

The number of components m was equal to 3 for pure NiO and 4 for $Ni_cMg_{1-c}O$. They corresponded to oxygen atoms of the first shell, nickel and magnesium atoms of the second shell and oxygen atoms of the third shell. Thus we used 12 and 16 fitting parameters (four (N_i, R_i, σ_I^2, ΔE_{0i}) for each shell) that is less than the number of independent data points $N_{ind} \approx 20$ ($N_{ind} = 2\Delta k \Delta R / \pi + 2$ where Δk and ΔR are respectively the widths in k and R space used in the fit[12]).

3. RESULTS AND DISCUSSION

The earlier observations in the optical absorption and luminescence spectra of the $Ni_cMg_{1-c}O$ monocrystals, grown by the chemical transport reaction method (the "sandwich" technique) on MgO single crystal substrates,[1,13] show an evidence of the distortion of the local environment around nickel

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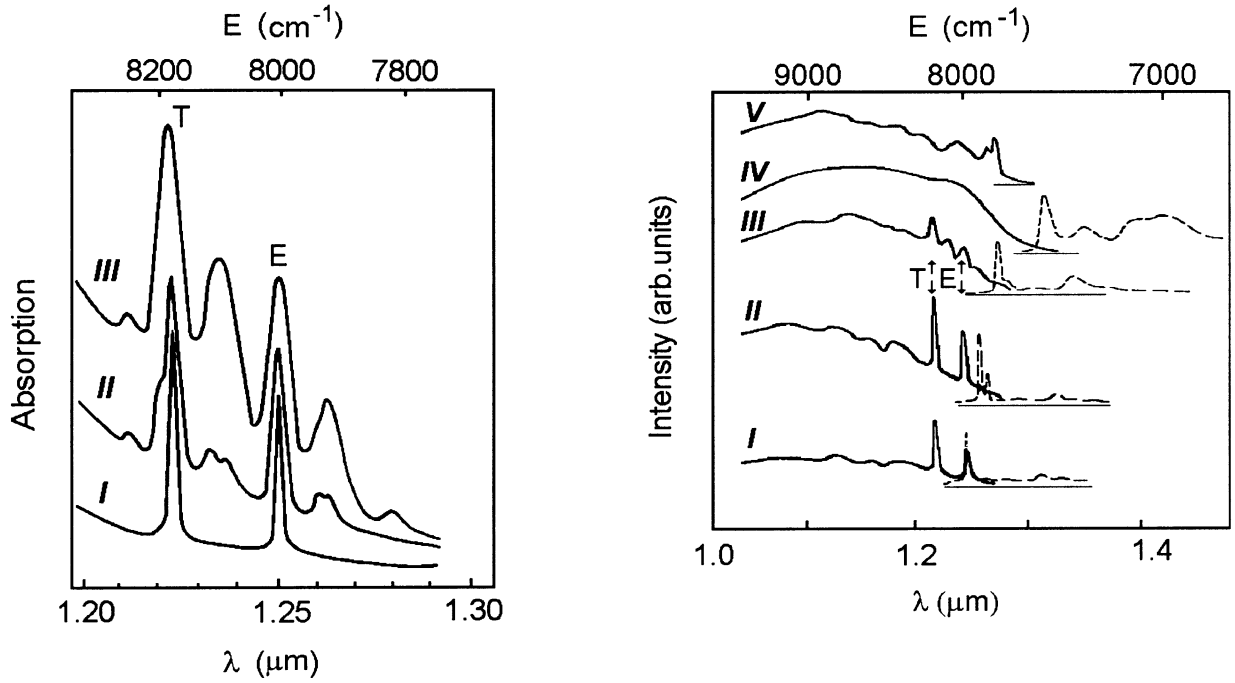

Fig. 2. Left panel: optical absorption spectra of Ni^{2+} ions in monocrystals $Ni_cMg_{1-c}O$ (*I* - c=0.01, *II* - c=0.05, *III* - c=0.1) measured at T=15 K. The lines corresponding to the transitions $^3A_{2g}(F) \rightarrow T(^3T_{2g})$ and $^3A_{2g}(F) \rightarrow E(^3T_{2g})$ are marked by T and E, respectively. Right panel: optical absorption at T=80 K (solid lines) and luminescence at T=10 K (dashed lines) spectra of Ni^{2+} ions in monocrystals $Ni_cMg_{1-c}O$ (*I* - c=0.01, *II* - c=0.05, *III* - c=0.1, *IV* - c=0.6, *V* - c=1.0) measured at T=15 K.

ions. The optical absorption spectra in the energy range of 7800-8300 cm^{-1} correspond to $^3A_{2g} \rightarrow {}^3T_{2g}$ magneto-dipole transition at Ni^{2+} sites and consist of two zero-phonon lines at 8005 and 8182 cm^{-1} (Fig. 2). The same zero-phonon transitions occur in the luminescence spectra.[1] Previously one has explained these two lines by the spin-orbit splitting.[14] However, according to the theoretical calculations, there should be four zero-phonon lines at 8011, 8177, 8563 and 8720 cm^{-1} with the relative intensities equal to 0.677, 1.000, 0.790 and 0.235, respectively, while only two lines at 8005 and 8182 cm^{-1} with the relative intensities equal to 0.645, 1.000 were observed in the experiment.[14] Therefore we suppose that these lines are due to the splitting of $^3T_{2g}$ excited state by a crystal field acting on nickel ions located at the off-center positions.

The additional lines, appearing in this energy range at the nickel concentration c>0.01 (left panel in Fig. 2) and related to the zero-phonon electron transitions, support the presence of the exchange coupled pairs (the so-called 90°-pairs) of Ni^{2+} ions.[1,13] The maximum number of the isolated pairs appears at the concentration c=0.05.[15]

The results of the EXAFS spectra analysis show that the coordination number N_1 =6.0±0.5 and the DW factor σ_1^2=0.0038±0.0007 $Å^2$, related to oxygen atoms of the first shell, remain constant upon

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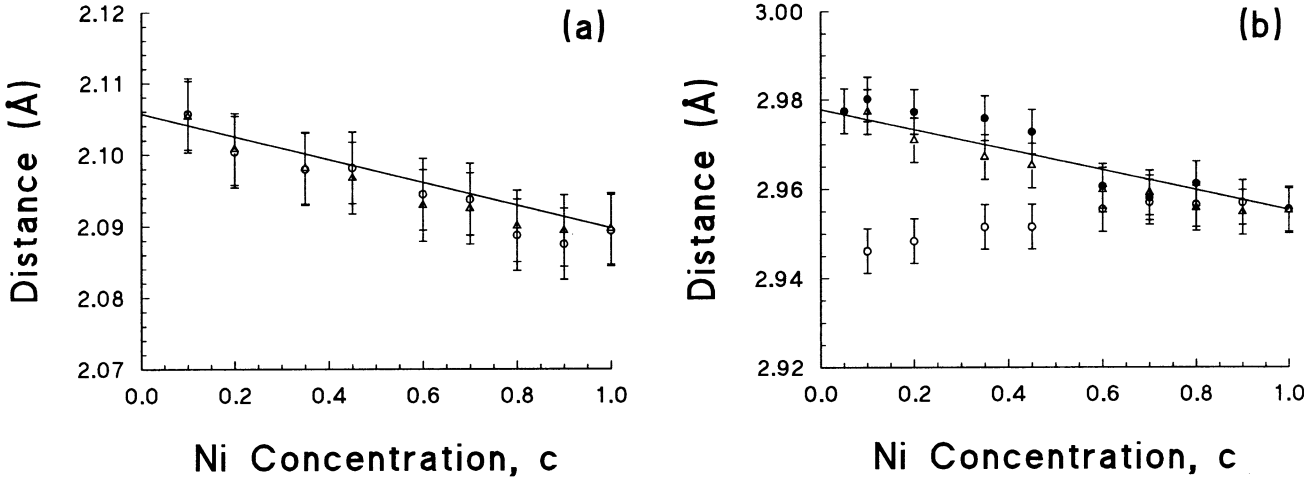

Fig. 3. Variation of the interatomic distances Ni–O (a), Ni–Ni (O) and Ni–Mg (●) (b) with the composition. Their values calculated in VCA from the average crystal lattice parameter, obtained by XRD[1,2] (—) and EXAFS (Δ), is also shown.

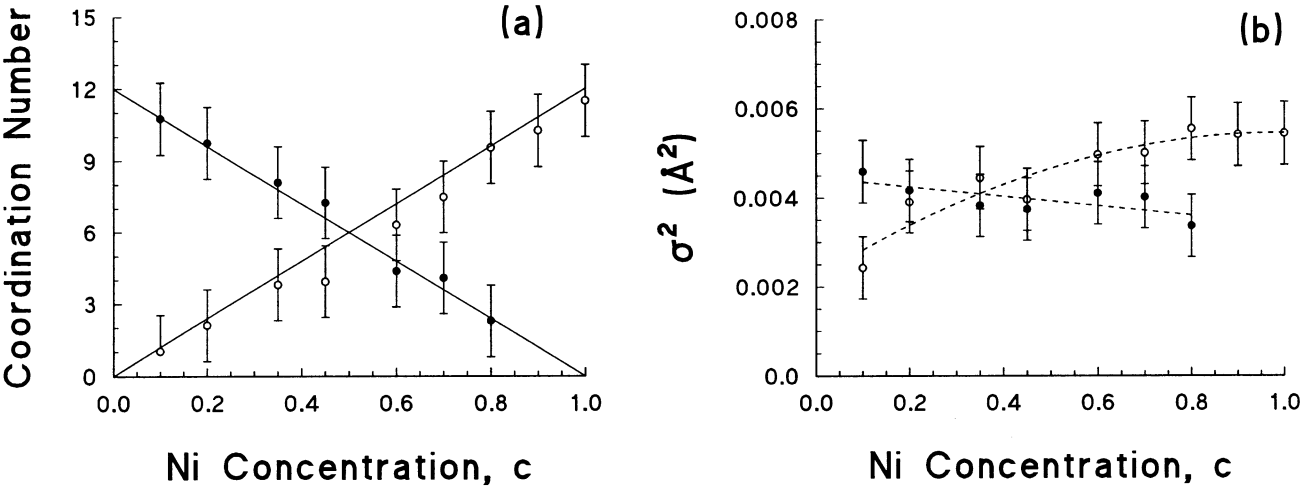

Fig. 4. Variation of the number of Ni and Mg ions (a) and the Debye-Waller factors for the Ni–Ni (O) and Ni–Mg (●) atom pairs (b) in the second shell with the composition. Solid lines in (a) correspond to the expected number of Ni and Mg ions in accordance with the formal composition. Dashed lines in (b) are guides for eye.

dilution within the error bar of the experiment. The value of the ΔE_0 correction for each shell was nearly constant within ±1.5 eV. The variations of other structural parameters versus c are shown in Figs. 3 and 4. Note that the change in the number of nickel and magnesium ions in the second shell (Fig. 4(a)) correlates well with the random distribution model.

The variation of the lattice parameter $a(c)$ in $Ni_cMg_{1-c}O$, determined by XRD,[1,2] is linear. It can be interpreted using the Vegard's law or the virtual crystal approximation (VCA). The Vegard's law states that the lattice parameter of the solid solution is equal to the additive sum of the lattice parameters of

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individual components weighted by concentration of each part. In this model, the values of bond lengths Ni–O and Mg–O are considered to be constant as in NiO and MgO, respectively. In VCA, the atoms are located on the ideal lattice sites of the average unit cell, and average values for bond lengths, bond ionicity, atomic potentials, etc. are assumed.

The Ni–O distance varies linearly upon dilution (Fig. 3(a)) in agreement with VCA. On the contrary, the variation of the Ni–Ni and Ni–Mg distances differ strongly from the ones expected in VCA (Fig. 3(b)). The dependence of the Ni–Mg distance from the composition has a break at $c \approx 0.6$ and is nearly constant below and above this concentration. The values of the Ni–Mg distance are higher than the ones expected in VCA at $c<0.6$ and comparable to them at $c>0.6$. The Ni–Ni distance is almost constant at $c>0.6$ and slightly decreases upon dilution. The values of the Ni–Ni distance are close to the ones expected from the Vegard's law but are always smaller than the ones expected in VCA. These results can be explained by a strong NN interactions of nickel ions[2,8] due to that upon dilution they tend to shift from the center of the oxygen octahedron. This process leads at low nickel concentration to formation of the Ni–Ni coupled pairs.[8,16] A shift of nickel ions to the off-center position is also favorable due to the difference of the ionic radii of Mg^{2+} and Ni^{2+} ions, which are, (taking, according to Goldschmidt, the radius of oxygen ion equal to 1.32 Å) 0.79 and 0.77 Å, respectively. As a result, when the lattice constant increases upon dilution, the nickel ions, having smaller size than magnesium ions, become more mobile and are able to displace out of the octahedron center.

To understand why the EXAFS results, opposite to the ones obtained by XRD, do not follow completely to neither the Vegard's law nor VCA, one should remember that the lattice parameter $a(c)$ is calculated from the diffraction pattern given by different crystallographic planes. Therefore, the value of a is averaged over all crystallographic directions and, thus, one should compare it with the analogous quantity given by EXAFS. From the obtained distances up to the first and the second shells, we calculated the average lattice parameter determined from EXAFS data as

$$a_{\mathrm{EXAFS}} = \left[2R(\mathrm{Ni}-\mathrm{O}) + 2(cR(\mathrm{Ni}-\mathrm{Ni}) + (1-c)R(\mathrm{Ni}-\mathrm{Mg}))\cos(45^\circ)\right]/2$$

where the first term in the square brackets corresponds to the lattice constant along the $\langle 100 \rangle$ directions and the second term corresponds to the lattice constant along the $\langle 110 \rangle$ directions. It is interesting to note that although the variation of the Ni–Ni and Ni–Mg distances does not obey VCA, the average lattice parameter, obtained from EXAFS data for the first and the second shells, does, and it is in good agreement with the one calculated from XRD data[1,2] (see triangles and solid lines in Fig. 3).

The behaviour of the Ni–Ni and Ni–Mg interatomic distances correlates with the variation of the DW factors for Ni–Ni and Ni–Mg atom pairs (Fig. 4(b)). At high nickel concentration $c>0.35$, the Ni–Ni DW factor dominates the Ni–Mg one since the magnesium ions, having larger size, are squeezed in the NiO lattice. At low nickel concentration $c<0.2$, the Ni–Mg DW factor dominates the Ni–Ni one since it increases due to the static disorder caused by the off-center position of nickel ions while the Ni–Ni DW factor decreases owing to the strong NN exchange interactions. Apparently, the cross point of the DW factor dependences at $c \approx 0.35$ can correlate with the experimental percolation threshold $c_{\mathrm{perc}} \approx 0.31$ below which the NN exchange interaction becomes important compared to the NNN.[2] Note that also the decrease of the Ni–Ni distance occurs below that concentration (Fig. 3(b)). However, this question requires further more accurate investigations.

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Now we compare the obtained results with the magnetic phase diagram.[8] Since all EXAFS measurements were performed at room temperature, one should look at the cut of the diagram along the line T ≈ 300 K. There two special points exist upon dilution:[8] at c=0.8, the destruction of the infinite antiferromagnetic domain structure is observed however the solid solution remains antiferromagnetic, while at c=0.6, the value of the Néel temperature T_N crosses the room temperature and the transition from antiferromagnetic to paramagnetic phase occurs. The EXAFS results show that above c=0.6 the distances Ni–Mg and Ni–Ni are nearly the same but at c<0.6 the difference between them increases rapidly (Fig. 3(b)). This correlates well with the neutron diffraction data:[8] it was found that the (1/2 1/2 1/2) magnetic peak has no detectable broadening above c=0.6 and its width increases rapidly below this concentration that can be explained by the presence of two different distances within the metal sub-lattice at c<0.6 (Fig. 3(b)).

4. SUMMARY AND CONCLUSIONS

In this work we carried out the x-ray absorption spectroscopy study of $Ni_cMg_{1-c}O$ ($0.01 \le c \le 1$) solid solutions on the Ni K-edge.

We found that opposite to the lattice parameter obtained by XRD, the interatomic distances given by EXAFS do not follow completely to neither the Vegard's law nor the virtual crystal approximation (VCA). However, the average lattice parameter obtained from EXAFS data for the first and the second shells agrees well with the one calculated from XRD data.[1,2]

In more detail, the results of the EXAFS analysis are as follow.

The average Ni–O distance increases upon dilution in agreement with VCA, and the number of nickel and magnesium ions in the second coordination shell of nickel varies in agreement with the random distribution model.

Nickel ions are located in the distorted local environment and displace upon dilution to the off-center positions. The nickel displacements occur due to the NN exchange interactions between any of two Ni^{2+} ions and are favored by the increase of the lattice parameter at small c values. The average Ni–Ni distance remains unchanged at c>0.6 and decreases slightly at low nickel concentration. The observed off-center position of nickel ions is also supported by the Debye-Waller factor variations. It is also in good agreement with the results of the optical absorption and luminescence measurements.[12] The dependence of the Ni–Mg distance from the composition has a break at c≈0.6 and is nearly constant below and above this concentration. This correlates well with the point of the transition from antiferromagnetic to paramagnetic phase.

5. ACKNOWLEDGMENTS

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