

Composition dependence of the lattice parameter in $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ solid solutions

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Abstract. We present an accurate x-ray powder diffraction study of stoichiometric $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ solid solutions performed using an internal-standard method. The results obtained allowed us to establish for the first time that the composition dependence of the lattice parameter $a(c)$ is not linear, as had been asserted, and interpreted within Vegard's model, in previous works. A new model, which is able to explain both the $a(c)$ behaviour and the variation of the local structure around nickel ions, obtained previously by x-ray absorption spectroscopy (Kuzmin A, Mironova N, Purans J and Rodionov A 1995 *J. Phys.: Condens. Matter* **7** 9357), is suggested and discussed.

1. Introduction

Diluted antiferromagnets represent an interesting class of materials whose crystallographic structure is closely related to their magnetic properties [1]. Recently, a correlation between long- and short-range order for solid solutions with face-centred-cubic (fcc) magnetic sublattices has been reviewed for a number of zinc-blende- and rock-salt-type compounds [2]. In these systems, depending on the type of the host-lattice packing, the cation/anion radii ratio and the difference in size of the ions, the ordered average crystal lattice experiences various local distortions, which are successfully probed by x-ray absorption spectroscopy (XAS) [1]. Therefore it is of great interest to understand whether such local distortions can also affect the values of the solid-solution lattice parameters determined from powder diffraction data.

A series of the $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ solid solutions provide examples of crystallographic structure intensively studied by x-ray diffraction (XRD) [3–7] and XAS [7–9]. Due to the small difference (about 0.02 Å [10]) between the ionic radii of Ni^{2+} and Mg^{2+} ions, they readily substitute for each other, so a continuous series of $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ solid solutions, with $0 < c < 1$, can be prepared. Up to now, it has been believed that the lattice parameter $a(c)$ of the $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ system depends linearly on the composition and follows Vegard's rule

$$a(c) = ca_{\text{NiO}} + (1 - c)a_{\text{MgO}}$$

(references [3–7].) However, the results of the recent Ni K-edge XAS studies [8, 9] suggested strong deviation of the local structure around nickel ions from Vegard's model: it was observed that whereas the interatomic Ni–Ni₂ distance (the subscript indicates the coordination shell number) remains nearly constant at all concentrations, the Ni–O₁

and Ni–Mg₂ distances increase linearly upon dilution of the nickel oxide, i.e. when c decreases. Such behaviour was explained by an off-centre displacement of nickel ions [8]; this interpretation also agrees with the results of low-temperature optical absorption and luminescence measurements [9, 11], for which displacements of nickel ions could explain why the zero-phonon-line splitting occurs. Thus it becomes important to understand the reason for the ‘disagreement’ between the XRD and the XAS data available in the literature.

In this paper, we present for the first time an accurate XRD study of Ni _{c} Mg_{1- c} O solid solutions performed using an internal-standard method. Our results unambiguously show that the composition dependence of the lattice parameter $a(c)$ in Ni _{c} Mg_{1- c} O deviates from the linear one assumed within Vegard’s model. To explain the $a(c)$ behaviour, we suggest a new model, which also agrees with the XAS data from our previous work (reference [8]).

2. Experimental details

Solid solutions of Ni _{c} Mg_{1- c} O ($c = 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$) were prepared from the appropriate amounts of aqueous solutions of Mg(NO₃)₂·6H₂O and Ni(NO₃)₂·6H₂O salts which were mixed and slowly evaporated. The remaining dry ‘flakes’ were heated up to 500–600 °C to remove NO₂ completely. The polycrystalline solid solutions obtained were powdered and annealed for 100 h at a temperature of 1200 °C in air and then quickly cooled down to room temperature. The pure NiO ($c = 1$) and MgO ($c = 0$) were obtained by thermal decomposition of the above-mentioned salts. Thus-obtained Ni _{c} Mg_{1- c} O powders with $c > 0$ have greenish colour, whose intensity depends on the nickel content and varies from green for $c = 1$ to light green for small c -values. Pure MgO is colourless.

The greenish colour of the Ni _{c} Mg_{1- c} O solid solutions can be used as a ‘fingerprint’ of their stoichiometry [12, 13]. Additionally, the composition of our samples was probed by instrumental neutron-activated analysis [14, 15], and it was confirmed [14] that the content of nickel in the samples was in agreement with the stoichiometric one within $\pm 0.01\%$. Note that the Ni _{c} Mg_{1- c} O samples with $c > 0$ were the same as had been used in XAS and optical measurements in [8, 9]. The XAS results [8], which did not reveal any deviation in the coordination numbers of nickel ions within the first and second coordination shells in the series, also prove the stoichiometry of the solid solutions.

All of the samples were annealed for four hours at 500 °C before diffraction measurements were made. The samples for XRD study were prepared by homogeneous mechanical mixing of finely ground Ni _{c} Mg_{1- c} O and polycrystalline silicon powder. The mixtures, in a quantity around 1–2 g, were back-pressed into a copper sample holder. Diffraction patterns were recorded using a Bragg–Brentano powder diffractometer ($\theta/2\theta$ scans) with a graphite monochromator in the diffracted beam for elimination of sample fluorescence. A conventional tube with a copper anode (Cu K α radiation) was used as the x-ray source. The measurements were performed at room temperature over the angular range $2\theta = 25\text{--}100^\circ$ in steps of $\Delta(2\theta) = 0.02^\circ$. The temperature during the measurements was unchanged within $\pm 2^\circ\text{C}$, leading to an uncertainty in the determination of the lattice parameter of about 0.003%, or less than $\pm 1.3 \times 10^{-4}$ Å, as estimated from the coefficient of linear expansion ($(11.4/15.6) \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for MgO and $(12.0/12.6) \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for NiO [15]).

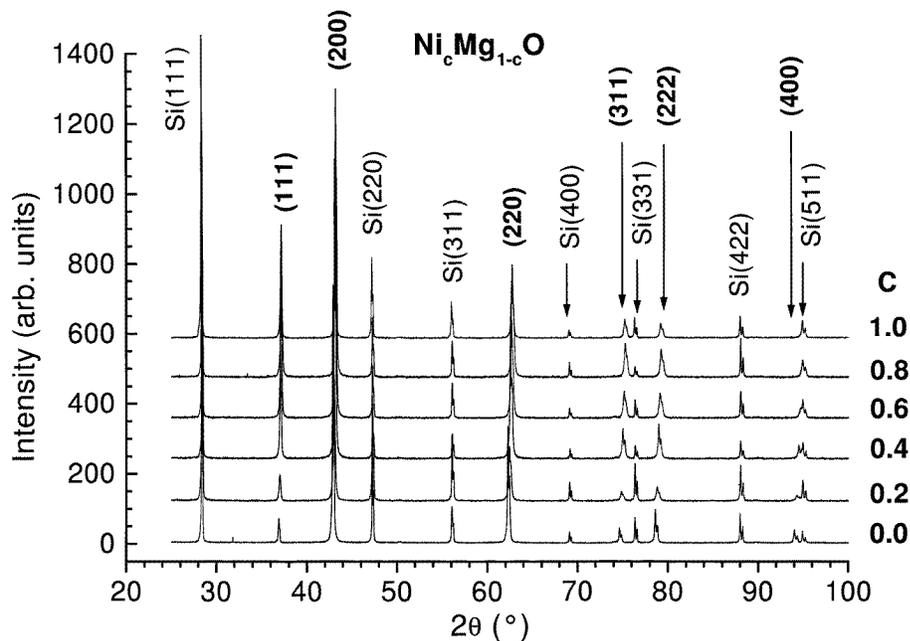


Figure 1. Powder diffraction patterns of $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ solid solutions mixed with crystalline silicon powder. Only a few spectra are shown for the sake of clarity.

3. Results and discussion

The XRD patterns obtained are presented in figure 1. The observed splitting of the diffraction lines at high angles ($2\theta > 45^\circ$) is due to the $\text{Cu } K\alpha_1\text{-}K\alpha_2$ doublet. As can be seen, crystalline silicon serves as a perfect internal standard in our case, since peaks due to silicon do not overlap the ones from the $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ system for angles $2\theta < 90^\circ$ and they are uniformly distributed throughout the scattering angle range. One can notice strong variation of the (111) peak intensity for solid solutions, which occurs due to the difference between the x-ray scattering intensities of the nickel and magnesium sublattices. The intensity of the (111) peak in compounds with the NaCl-type structure, which is the structure type of the $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ series, depends on the difference between the number of electrons of the anions and cations [16]: this explains the smaller magnitude of the (111) peak for MgO as compared to that for NiO.

The XRD patterns shown in figure 1 were least-squares fitted by a set of pseudo-Voigt functions taking into account both $K\alpha_1$ and $K\alpha_2$ components [17]. The thus-determined peak positions were utilized in the least-squares refinement of the $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ lattice parameters $a(c)$ (table 1) by the XLAT code [18] using silicon-related peaks as the internal standard ($a_0(\text{Si}) = 5.430880 \text{ \AA}$; JCPDS-ICDD PDF card No 27-1402). The fitting uncertainty was less than $\pm 0.0002 \text{ \AA}$ in all cases. Thus, the main contribution to the error of the $a(c)$ values was due to the uncertainty in the angle determination: it was estimated to be equal to about $\pm 0.0007 \text{ \AA}$ for $c \leq 0.7$ and $\pm 0.0009 \text{ \AA}$ for $c > 0.7$ due to complete overlap of Si(511) and $\text{Ni}_c\text{Mg}_{1-c}\text{O}(400)$ reflections for $c > 0.7$ (figure 1). Note that several measurements for each sample led to differences in the calculated lattice parameters of less than $\pm 0.0005 \text{ \AA}$ —the value being half that of the total uncertainty Δa .

Table 1. The lattice parameter $a(c)$ in $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ solid solutions determined using an internal-standard method. Δa takes into account the uncertainty of the angle determination ($\sim \pm 0.0007 \text{ \AA}$ for $c \leq 0.7$ and $\sim \pm 0.0009 \text{ \AA}$ for $c > 0.7$), the fitting uncertainty ($\leq \pm 0.0002 \text{ \AA}$) and the temperature-variation effect ($< \pm 0.00013 \text{ \AA}$).

c	$a(c) \pm \Delta a \text{ (\AA)}$	Reference
MgO	4.213	JCPDS-ICDD PDF card No 4-829
	4.211	[6]
0.0 (MgO)	4.2123 ± 0.0010	This work
0.05	4.2108 ± 0.0010	This work
0.1	4.2074 ± 0.0010	This work
0.2	4.2030 ± 0.0010	This work
0.3	4.1999 ± 0.0010	This work
0.4	4.1963 ± 0.0010	This work
0.5	4.1920 ± 0.0011	This work
0.6	4.1891 ± 0.0011	This work
0.7	4.1863 ± 0.0011	This work
0.8	4.1830 ± 0.0012	This work
0.9	4.1801 ± 0.0012	This work
1.0 (NiO)	4.1773 ± 0.0012	This work
NiO	4.1769	JCPDS-ICDD PDF card No 4-835
	4.177	[19]
	4.1765	[20]
	4.180	[6]

The values obtained for the lattice parameters $a(c)$ and their total uncertainties Δa are reported in table 1. As can be seen, our results for pure NiO and MgO are in excellent agreement with the known values published by other authors [6, 19, 20]. Also, the values of a for pure NiO correspond in all cases to the ideal cubic cell which in reality exists in the paramagnetic phase above the Néel temperature $T_N = 523 \text{ K}$ [21]. According to [20, 22], the NiO structure at room temperature experiences rhombohedral distortion; however, this is so small that appreciable splitting of the reflections can only be detected at high angle values (above 129°).

The variation of the lattice parameter $a(c)$ versus the nickel concentration c is shown in figure 2(a). A deviation is observed between the experimental points and Vegard's model (VM), especially for the intermediate concentrations. By looking at the difference $a(c) - a_{\text{VM}}(c)$ in figure 2(b), one can see that it is larger than the estimated uncertainty of $a(c)$, and its maximum value reaches about -0.002 \AA .

Assuming statistical distribution of nickel and magnesium ions, the lattice parameter $a(c)$ of the $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ system is given by

$$a(c) = c^2 a_{\text{NN}}(c) + 2c(1-c) a_{\text{NM}}(c) + (1-c)^2 a_{\text{MM}}(c) \quad (1)$$

where the first term represents the contribution from all Ni–Ni atom pairs, the second term is due to all Ni–Mg (Mg–Ni) atom pairs and the last term is due to all Mg–Mg atom pairs (here only the metal–metal pairs located along unit-cell edges in the $\langle 100 \rangle$ directions are considered). In terms of the nearest-neighbour metal–oxygen bonds, the lattice parameters are $a_{\text{NN}} = 2R(\text{Ni–O})$, $a_{\text{MM}} = 2R(\text{Mg–O})$ and $a_{\text{NM}} = R(\text{Ni–O}) + R(\text{Mg–O})$. Note also that $a_{\text{NN}}(1) = a_{\text{NiO}}$ and $a_{\text{MM}}(0) = a_{\text{MgO}}$.

In Vegard's model, the values of the Ni–O and Mg–O bond lengths in the solid solutions

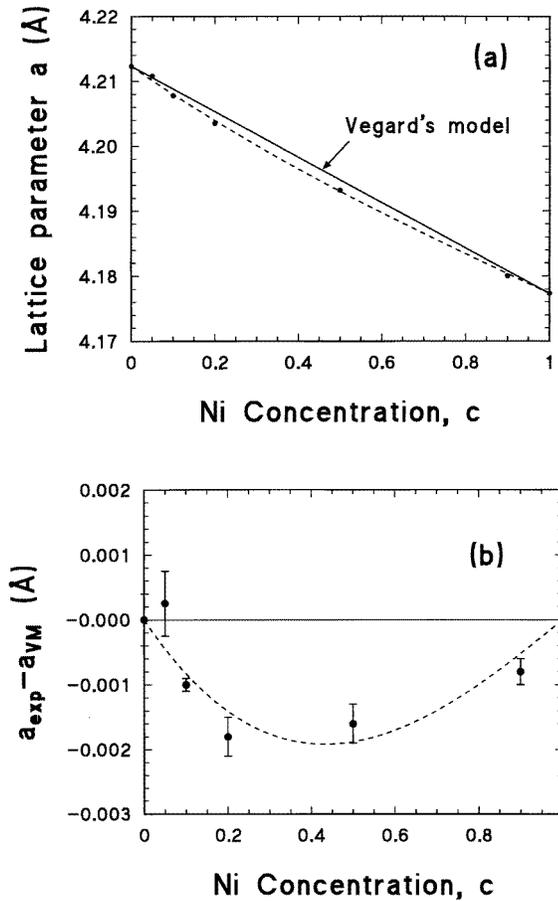


Figure 2. (a) The variation of the lattice parameter $a(c)$ (full circles) in $Ni_cMg_{1-c}O$. (b) The difference between the values of the lattice parameter $a(c)$ obtained and the prediction of Vegard's model $a_{VM}(c)$. In both panels, solid lines represent Vegard's model, and dashed lines correspond to the model suggested in the present work and described by equation (3).

are considered to be constant as in NiO and MgO. Therefore, one has $a_{NN}(c) = a_{NiO}$, $a_{MM}(c) = a_{MgO}$ and $a_{NM}(c) = (a_{NiO} + a_{MgO})/2$, so, from equation (1), the lattice parameter $a(c)$ of the solid solution becomes equal to the additive sum of the lattice parameters of individual components weighted with the concentrations of each part:

$$a_{VM}(c) = ca_{NiO} + (1 - c)a_{MgO}. \quad (2)$$

The same expression for the lattice parameter can be obtained in the virtual-crystal approximation (VCA) which assumes that the atoms are located on the ideal-lattice sites of the average unit cell, and average values for the bond lengths, bond ionicity, atomic potentials etc are considered. Therefore, in the framework of the VCA, the metal–oxygen (MO) and metal–metal (MM) distances vary as the lattice parameter $a(c)$ does, and one has

$$a_{NN}(c) = a_{NM}(c) = a_{MM}(c) = ca_{NiO} + (1 - c)a_{MgO}.$$

Thus, Vegard's model and the VCA model represent two extreme cases from the short-range-order point of view based on the contradictory notions of the invariant radii, introduced

by Pauling [23], and of the completely relaxed bonds, respectively. However, they both suggest linear dependence (equation (2)) of the lattice parameter on the composition, which is not consistent with the results for $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ solid solutions obtained in the present work (figure 2).

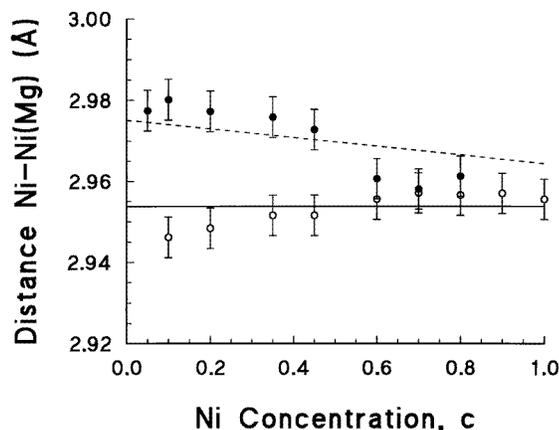


Figure 3. The variation of the Ni–Ni₂ (open circles) and Ni–Mg₂ (full circles) interatomic distances between the nickel ions and the Ni/Mg ions located in the second coordination shell according to the XAS data taken from [8]. Solid and dashed lines correspond to Ni–Ni₂ and Ni–Mg₂ distances calculated according to the model suggested in the present work and described by equation (3).

To explain the experimental behaviour of $a(c)$, we suggest the following model based on equation (1). It is known from the XAS data [8] that: (1) the average Ni–Ni₂ interatomic distance remains nearly constant at all compositions; therefore we suppose that $a_{\text{NN}}(c) = a_{\text{NiO}} = \text{constant}$; and (2) the average Ni–Mg₂ interatomic distance varies around the values given by the VCA model (figure 3); therefore we approximate its composition dependence by a linear function $a_{\text{NM}}(c) = f(b_1 + b_2c)$ (note that the coefficient b_2 should be negative to achieve an increase of the Ni–Mg₂ distance when c decreases). Also, taking, according to Shannon [10], the radius of the oxygen ion equal to 1.40 Å, one obtains that the ionic radius of the magnesium ion, $R(\text{Mg}^{2+}) \simeq 0.71$ Å, is larger than that of the nickel ion, $R(\text{Ni}^{2+}) \simeq 0.69$ Å. Therefore it is reasonable to assume that the larger magnesium ions are squeezed by the oxygen sublattice and, thus, that they are always located at the regular sites of the crystal lattice. As a result, the composition dependence of the Mg–Mg interatomic distance should follow the lattice parameter and can be approximated by the expression used in the VCA model: $a_{\text{MM}}(c) = ca_{\text{NiO}} + (1 - c)a_{\text{MgO}}$. Finally, one gets the expression for the lattice parameter $a(c)$ of $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ in the form

$$a(c) = c^2 a_{\text{NiO}} + 2c(1 - c)(b_1 + b_2c) + (1 - c)^2(ca_{\text{NiO}} + (1 - c)a_{\text{MgO}}) \quad (3)$$

with a_{NiO} and a_{MgO} defined in table 1 and $b_2 < 0$. The coefficients b_i were determined by a least-squares fit of equation (3) (see the dashed lines in figure 2) to the composition dependence of $a(c)$ obtained by XRD: they are $b_1 = 4.206 \pm 0.001$ Å and $b_2 = -0.014 \pm 0.002$ Å. It is important that, unlike Vegard's model and the VCA model, the suggested model (equation (3)) is in good agreement with our XRD data and also satisfies the XAS results from [8] (figure 3).

Finally, it is interesting to estimate the type of local deformation around impurity ions in MgO and NiO host lattices. To do this, we compare the values of a_{NM} , calculated from the coefficients b_i , with the host-lattice parameter $a(c)$ at $c = 0$ and $c = 1$, i.e. when the impurity Ni (Mg) ion can be considered to be isolated in the host MgO (NiO) matrix. At $c = 0$, $a_{\text{NM}} = 4.2075 \text{ \AA}$ is smaller than $a_{\text{MM}} = a_{\text{MgO}} = 4.2123 \text{ \AA}$ but it is larger than the sum (4.1948 \AA) of the undistorted Ni–O and Mg–O distances. This means that in Ni-doped MgO crystals, the local environment around nickel impurities relaxes partially in the direction of the impurity ions, i.e. the host lattice shrinks around nickel ions, as they have ionic radii smaller than those of the magnesium ions. This conclusion is consistent with the result of the Ni K-edge XANES analysis reported in [24] where it was observed that the overlap between oxygen 2p and nickel 3d orbitals increases at small c -values. At $c = 1$, $a_{\text{NM}} = 4.1925 \text{ \AA}$ is larger than $a_{\text{NN}} = a_{\text{NiO}} = 4.1773 \text{ \AA}$ but it is smaller than the sum of undistorted Ni–O and Mg–O distances. This means that in Mg-doped NiO crystals, the local environment around magnesium impurities relaxes partially in the direction away from the impurity ions, i.e. magnesium ions move the surrounding host lattice aside. Thus, substituting Mg (Ni) ions induce local deformations of the host NiO (MgO) lattice, and the type of deformation is in agreement with the one which can be expected from the relative values of the ionic radii.

4. Summary and conclusions

The lattice parameter $a(c)$ of stoichiometric $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ solid solutions was determined by x-ray powder diffraction using an internal-standard method. It was found for the first time that the composition dependence of the lattice parameter $a(c)$ deviates from the linear Vegard model obtained in previous work [3–7].

To explain this result, a combination of the lattice parameter $a(c)$ determined by XRD in the present work with the values of the Ni–O, Ni–Ni and Ni–Mg interatomic distances obtained by us previously using x-ray absorption spectroscopy [8, 9] was used to derive a new structural model (see equation (3)), which takes into account the off-centre displacements of nickel ions suggested previously in [8, 9, 11]. The proposed model is in good agreement with the experimentally observed variations of the long-range order and local atomic structure in $\text{Ni}_c\text{Mg}_{1-c}\text{O}$ as a function of composition.

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