Studies of $Co_xMg_{1-x}O$ Solid Solutions Using Laboratory EXAFS-Spectrometer

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Studies of the local electronic structure and the short-range order in solid solutions $Co_xMg_{1-x}O$ with x equal from 0.02 to 1.00 have been carried out on the Co K-edge X-ray absorption spectra measured using the laboratory EXAFS-spectrometer. A non-monotonous change of the Co-O distance in the first coordination shell with the bent at $x=0.5$ has been established. The second coordination shell of cobalt has been formed by cobalt and magnesium atoms with a distribution close to statistical.

§1. Introduction

The CoO-MgO binary system forms a continuous series of solid solutions and at any composition has a face-centered cubic crystalline lattice of the NaCl type, the parameter of which according to X-ray diffraction data linearly depends on the composition.[1] The radii of Co (0.79 Å) and Mg (0.71 Å) cations strongly differ, therefore during the formation of solid solutions a static homogeneous deformation of the crystalline lattice and a local deformation created by the substituting ion should be observed.

The investigations of the $Co_xMg_{1-x}O$ system at $x=0.05$ by the EXAFS and XANES methods have been reported earlier.[2] It was established that at this concentration the Co^{2+} ions are statistically distributed in the MgO lattice.

In this work we present the EXAFS studies of the short-range order of the $Co_xMg_{1-x}O$ solid solutions in the range from $x=0.02$ to 1.00 on the Co K-edge using the laboratory EXAFS-spectrometer.[3] Both the XANES and EXAFS regions are considered. The dependence of the local order parameters and the fine structure of the absorption edge from the CoO concentration is discussed.

§2. Experimental and Data Analysis

Solid solutions $Co_xMg_{1-x}O$ with $x=0.02$, 0.05, 0.10, 0.20, 0.50, 0.90, 1.00 were prepared using ceramics technology by a solid phase reaction method as a result of decomposition of oxygen containing salts of magnesium and cobalt ($MeSO_4$, $MeCO_3$) at 1200°C temperature.[3] The polycrystalline samples were finely ground and deposited on an organic substrate with the layer thickness equal 5-20 μm.

The X-ray absorption spectra of the Co K-edge were measured using laboratory EXAFS-spectrometer created in the Institute of Solid State Physics (Riga) on the base of the standard diffractometer.[4] The Johann scheme with a bent crystal monochromator of the crystalline α-quartz ($10\bar{1}1$) was used to focus X-ray radiation from the molybdenum tube. The measurements were done at room temperature in transmission mode. The energy resolution was estimated equal to 6 eV. The total time of one measurement was in the range from 6 to 24 hours depending on the Co atoms concentration.

The standard procedure was used for the experimental EXAFS data treatment.[5] The analysis of the signals from the first two coordination shells was done in the single-scattering approximation that is allowed due to the close packing NaCl-type structure of $Co_xMg_{1-x}O$. For such structure, there are no contributions from the multiple-scattering processes in the range inside the first two shells.

§3. Results and Discussion

3.1 EXAFS analysis

The experimental EXAFS-spectra $\chi(k)k^2$ and their Fourier transforms (FT) are shown in Fig. 1. The high frequency noise component was taken away by the Fourier filtration of the EXAFS-signal in the interval
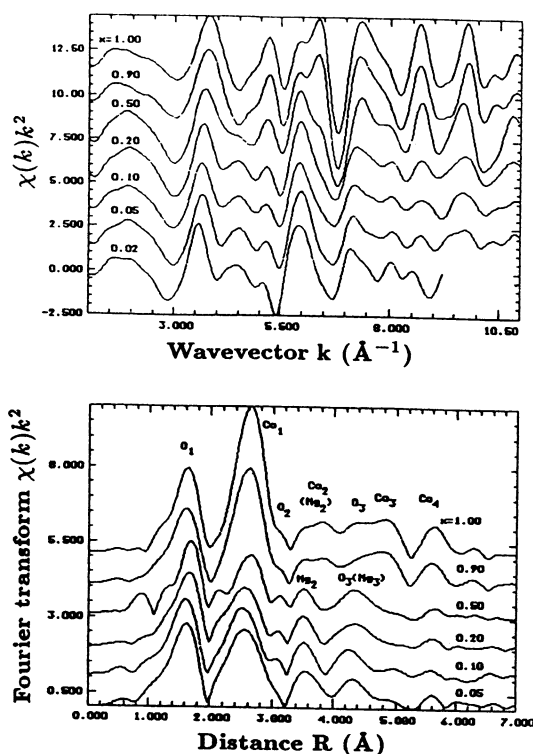
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Fig. 1. Experimental EXAFS spectra $\chi(k)k^2$ of the solid solutions $Co_xMg_{1-x}O$ (upper figure) and their Fourier transforms (lower figure). The first seven coordination shells are marked.

from 0 to 7 Å. One can see that the oscillations are very intensive even at low concentration of the Co atoms. Two main peaks, located at 1.5 Å (the first shell) and 2.5 Å (the second shell), are present in the FT of all samples.

The contribution from the first shell was separated by the back FT in the interval from 0.7 to 2.0 Å, and the Co-O distance was determined by the fitting procedure with the backscattering amplitudes and phases taken from refs. 6 and 7. The obtained results are shown in Fig. 2. One can see that the Co-O distance changes non-linearly within 0.02 Å interval with the bent at $x=0.5$. Other parameters, as the coordination number equal to 6 oxygen atoms and the Debye-Waller factor equal to 0.005 $Å^2$, did not change in the whole x range within the experimental error.

The second peak corresponds to 12 Co (Mg) atoms in the second coordination shell of cobalt. In Fig. 3 (at the top), the EXAFS-signals from the second coordination shell, separated by the back FT procedure in the interval from 2.0 to 3.2 Å, are presented. The decrease of the CoO concentration leads to the shift of the EXAFS-signal maximum to the lower energies, and, moreover, to an essential decrease of the peak's amplitude in the FT (see, Fig. 1). The analysis shows that this effect is connected with the interference of the backscattering
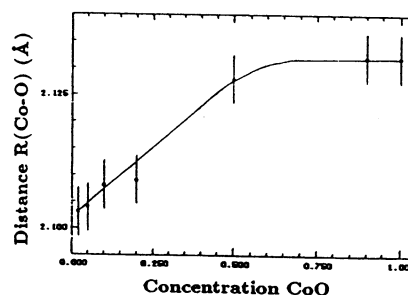

Fig. 2. The dependence of the Co-O distance in the first coordination shell from the concentration of the cobalt ions in the solid solutions $Co_xMg_{1-x}O$.
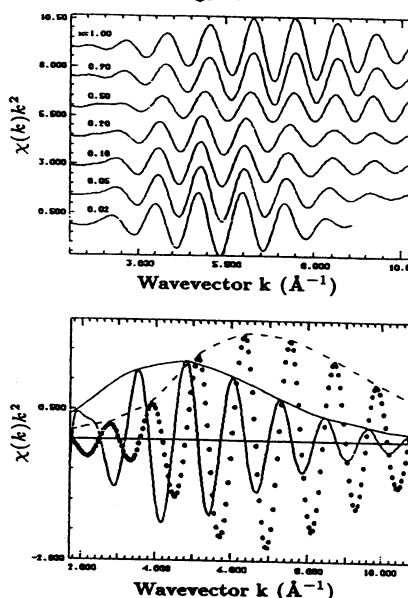

Fig. 3. Experimental EXAFS spectra $\chi(k)k^2$ for the second coordination shell (Co-Co(Mg)) (upper figure). Calculated EXAFS spectra $\chi(k)k^2$ for the Co-Mg (solid line) and Co-Co (circles) bonds (lower figure). One can see the difference between cobalt and magnesium backscattering amplitudes and phases.

signals from cobalt and magnesium atoms statistically distributed in the second shell. The cobalt and magnesium atoms differ essentially in the amplitude and phase of the photoelectron's backscattering[6] that can be observed in Fig. 3 (at the bottom) as the displacement of the modulus maximum of the EXAFS signal amplitude to the smaller wavevectors (from 8 $Å^{-1}$ at $x=1.00$ to 5.5 $Å^{-1}$ at $x=0.05$) and in the displacement of the positions of maxima and minima of the signal (the phase changes almost on 90 degree).

3.2 XANES analysis

In Fig. 4 the XANES spectra and their first derivatives for solid solutions $Co_xMg_{1-x}O$ with x from 0.02 to 1.00 are shown. In the region of the absorption edge it is possible to single out six features: A', A, B, C, D, E.

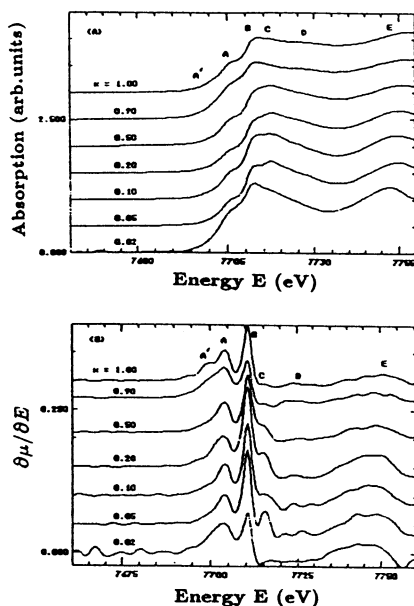The feature A', located before the main ab-

Fig. 4. XANES spectra of the Co K-edge (A) and their first derivatives $\partial\mu/\partial E$ (B) in the solid solutions $Co_xMg_{1-x}O$.

Fig. 5. XANES spectra of the Co K-edge in CoO. (Solid line - experiment, circles - the total signal, calculated in the single scattering approximation, from the atoms in the first, the second and the third coordination shells, dots - contribution of the third (oxygen) shell.)

§4. Summary and Conclusions

The X-ray absorption spectra of the Co K-edge in $Co_xMg_{1-x}O$ (with x from 0.02 to 1.00) solid solutions were studied using the laboratory EXAFS-spectrometer.

A non-linear change of the Co-O distance in the first coordination shell with the inflection at $x=0.5$ was established. It was found that the second coordination shell of cobalt is formed by the cobalt and magnesium ions with the distribution close to statistical.

The pre-edge part of the spectrum is not sensitive to the substitution of the magnesium for the cobalt. This means that cations in the second and the following coordination shells practically do not give any contribution to the p-character of excited states (the bottom and the middle parts of the conduction band). Above the absorption edge (the upper part of the conduction band) their substitution influences essentially on the shape of the absorption spectrum.

sorption edge corresponds to the transition $1s \rightarrow 3d(t_{2g}+e_g)[Co]+2p[O]$. In the dipole approximation the transitions of the ns $\rightarrow$ md type in a regular octahedron are forbidden, therefore the intensity A' is very weak and is due to the insignificant distortions of the octahedron of the first coordination shell by thermal vibrations and the mixing with the 2p states of oxygens.

The shoulder A located at the absorption edge corresponds in the atomic approximation to the forbidden transition $1s \rightarrow 4s$. Its high intensity is due to the mixing of the 4s and 4p cobalt states by the oxygen atoms located in the third coordination shell. In the multiple-scattering formalism, the shoulder A corresponds to the resonance scattering of the wave with the s-symmetry by the oxygen atoms in the third coordination shell.

The main maximum B corresponds to the allowed transition $1s \rightarrow 4p[Co]+2p[O]$. In the multiple-scattering approach the peak B is due to the resonance scattering of the photoelectron by oxygens in the first coordination shell. The feature C corresponds to the transition $1s \rightarrow 5p$ into delocalized p states of the conduction band. The substitution of magnesium ions by cobalt leads to the statistical distribution of both types ions in the cation sublattice and the decrease of the delocalization degree of the 5p states leading to the increase of the amplitude of the C peak. The bent D is owing to the resonance scattering of the photoelectron by oxygen atoms in the third coordination shell (Fig. 5). Peak E corresponds to the resonance scattering of the photoelectron by oxygen atoms in the first coordination shell.
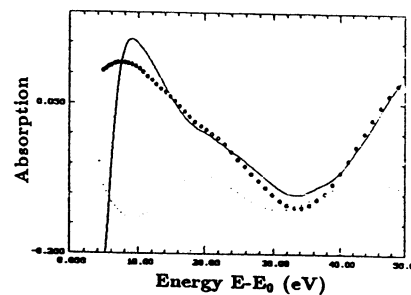
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