The cooperative Jahn–Teller effect and anti-isomorphic phases in Ni$_{1-x}$Co$_x$Cr$_2$O$_4$ solid solutions: Synchrotron X-ray diffraction study

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A R T I C L E   I N F O

Article history:
Received 28 April 2015
Received in revised form 9 June 2015
Accepted 17 June 2015
Available online 18 June 2015

Keywords:
A. Ceramics
C. X-ray diffraction
D. Phase transitions
D. Crystal field
D. Crystal structure

A B S T R A C T

A low-temperature high-resolution powder diffraction study has been carried out on a system of Ni$_{1-x}$Co$_x$Cr$_2$O$_4$ solid solutions with $x \leq 0.1$ down to 5 K. The tetragonal phase (I4$_1$/amd) with $c/a < 1$ was experimentally observed in Ni$_{0.9}$Co$_{0.1}$Cr$_2$O$_4$ below ~64 K. The new phase is anti-isomorphic to the well-known tetragonal phase of NiCr$_2$O$_4$. A unified phenomenological model has been applied to structural phase transitions in Ni$_{1-x}$Co$_x$Cr$_2$O$_4$ solid solutions. It shows that the appearing of such a phase is justified from a structural point of view. Analysis of atomic displacements confirms predictions of the symmetry-based model-free consideration.

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1. Introduction

The complex oxides AB$_2$O$_4$ with spinel type structure, which contain $d$ elements at the octahedral sites B, exhibit a broad diversity of physical properties. Such structures show complex magnetic phase diagrams; they are also superconductors, multiferroics, electrode materials, catalysts etc. In many cases their original properties relate to the structural peculiarity of spinels, which is the three-dimensional frustrated pyrochlore lattice formed by B-site ions. The existence of the large amount locally ordered or disordered spin, charge, orbital and atomic competing configurations possessing almost equal energies is one of the main features of such lattices [1–7].

In the chromium spinels ACr$_2$O$_4$ the Cr$^{3+}$ ions are almost always occupy octahedral positions due to the high energy of the crystal field. Consequently, spinels are good model systems for the creation of solid solutions with ions substitution in the tetrahedral positions.

Frustration of spins at low temperature causes magnetic phase transitions (A = Mg: $T_N = 12.5$ K [8]; Zn: $T_N = 12$ K [9] or 12.7 K [10]; Cd: $T_N = 7.8$ K [11–13]; Hg: $T_N = 5.8$ K [14,15]) accompanied by structural tetragonal and orthorhombic distortions. Low-temperature synchrotron X-ray [16] and neutron [10] diffraction studies revealed a tetragonal distorted structure for MgCr$_2$O$_4$ (space group I4$_1$/amd, $a = 5.89199(5)$ Å, $c = 8.31677(8)$ Å at 10 K). The corresponding structural transformation is very close or it even occurs simultaneously with magnetic phase transition. The low temperature high-resolution synchrotron X-ray diffraction data for MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ showed co-existence of tetragonal I4$_1$/amd and orthorhombic Fddd phases [17].

The physical behavior of the compounds is very complex and unusual for those spinels with magnetic ions in the tetrahedral A-positions. Examples of such spinels are CoCr$_2$O$_4$, FeCr$_2$O$_4$ and MnCr$_2$O$_4$. Frustration of the B-cation (pyrochlore) sublattice in these spinels leads to complex non-collinear magnetic structures with three magnetic sublattices: A, Cr$_1$, and Cr$_2$ [18]. The conical spin structure was observed in CoCr$_2$O$_4$, FeCr$_2$O$_4$ and MnCr$_2$O$_4$ at approximately $T_c = 27$ K, $T_s = 35$ K and $T_1 = 14$ K, respectively [1,19,20]. If A-cations are Jahn–Teller (JT) ions such as Cu$^{2+}$ and Ni$^{2+}$ in CuCr$_2$O$_4$ and NiCr$_2$O$_4$, as well as their solid solutions, then occurs the orbital degeneracy of electronic states, which can be lifted by cubic-to-tetragonal crystal structure distortions due cooperative JT effect. The magnetic geometrically frustrated system is...
possible only for spinels with cubic structure, because the tetrahedron of the pyrochlore sublattice becomes irregular after JT tetragonal distortion. Thus the situation for cubic and tetragonal spinels may be significantly different in the vicinity of magnetic transition temperature. Nevertheless, simultaneous magnetic and structural phase transitions were observed in CuCr2O4 and NiCr2O4 tetragonal spinels [21]. A large amount of work shows the strong impact of the cooperative Jahn–Teller effect on the structure and properties of materials with not only the variation of temperature but external hydrostatic pressure [22–24].

In this paper, we study the structural phase transitions in a system of Ni1− xCo xCr2O4 solid solutions with the mixed JT and non-JT magnetic ions at tetrahedral A-positions of the normal spinel structure. The tuning off JT mechanism of the removing of orbital degeneracy by reducing the concentration of JT ions in solid solution leads to unexpected structural states.

The system calls the additional interest due to the recent discovery of the spontaneous polarization in CoCr2O4 [19,25–27] and, in some members of solid solutions family [28], with already existing magnetic order. Thus, these materials can be classified as multiferroics, which are of great interest from the viewpoint of thus various applications. This applies especially to the second type multiferroic with coupling between the magnetic ordering and the spontaneous polarization according to the classification given in Ref. [29].

In our paper we experimentally follow temperature-concentration evolution of the crystal distortion in Ni1− xCo xCr2O4 solid solutions down to 5 K. Then, we briefly introduce a unified phenomenological model which predicts the possible structural phase states, regardless of the microscopic mechanism of its implementation, and showing coherency of theoretical predictions and experimental results. Finally, we discuss structure aspects of the corresponding structural phase transitions induced by the 2D irreducible representation Eg.

2. Experimental

2.1. Sample preparation

The samples Ni1− xCo xCr2O4 with x = 0, 0.005, 0.01, 0.015, 0.02, 0.1 were prepared following a standard solid state reaction procedure. The mixture of oxides, (1 − x)NiO−xCr2O4, was annealed at 1700 K for 3 h, then the pressurized cylindrical samples were annealed at 1850 K for 2 h. The resulting ceramic pellets were 10 mm in diameter and 2–3 mm thick. The sample composition was analyzed by energy dispersive spectroscopy. The average values for the composition of the spinel compounds were equal to the stoichiometry of oxides mixes with standard deviation less than 1 wt%.

2.2. X-ray diffraction

Temperature-dependent synchrotron X-ray powder diffraction data were collected at the BM01A beamline of the Swiss-Norwegian Beamlines, ESRF (Grenoble, France) using 2D Pilatus2M (Dectris) detector. The temperature was changing in the ramp mode from 90 K to 300 K with typical step of 1.4 K by open-flow Oxford Cryostream700+ system. The monochromatic beam at wavelength $\lambda = 0.682396 \, \text{Å}$ was slitted down to 300 × 300 μm². 200 μm diameter glass capillaries were used for mounting finely ground powder samples. The sample was rotated by 10 degrees. The sample-to-detector distance (D = 193 mm), the tilt angles of the detector and the wavelength were calibrated using LaB₆ NIST standard. The calibration and subsequent integration were performed using fit2D software [30].

Low temperature high-resolution synchrotron radiation powder diffraction patterns were collected at the powder diffraction station of the Swiss Light Source – Materials Science beamline (SLS-MS) on the solid-state silicon microstrip 1-D detector MyTHEN at an incident photon energy of 20 keV ($\lambda = 0.6204187 \, \text{Å}$). The sample was mounted in a Janis cryostat in 0.2 mm capillaries which spun at approximately 10 Hz during the 2θ scan to avoid preferred orientation and get better statistics. The sample-detector distance (D = 790 mm) and the detector parameters were calibrated using a Silicon reference powder sample.

Rietveld refinement was carried out using FullProf suit [31]. The refined parameters were the scale factor, unit cell dimensions, atomic coordinates, isotropic displacement parameters, profile parameters. The pseudo-Voigt profile was employed for the refinement of data.

3. Results

The structural phase states of outer members of the family of solid solutions serve as a good reference as they are well known and presented in detail in many papers. The structure of CoCr2O4 is cubic (space group Fd3m) up to 5 K [32]. NiCr2O4 undergoes two structural phase transformations with temperature decreasing. The first-order phase transition between the fcc (space group Fd3m, Z=8) and fct (space group I41/amd, Z=4, c/a > 1) structures is found to occur in the temperature range of 290–310 K. The second phase transition, between the tetragonal and orthorhombic phase, occurs at 70 K (see Refs. [21,33]). Fddd is a maximal nonisomorphic subgroup of I41/amd, which is derived from the parent Fd3m by loss of all three-fold rotation axes and part of the two-fold screw axes. In NiCr2O4, variable-temperature synchrotron x-ray diffraction measurements show additional structural changes below 30 K [21], in concurrence with anomalies in specific heat and susceptibility measurements of NiCr2O4 reported previously in the literature [34,21].

Diffraction data shows that the sample with x=0.02 contains about 1.3% admixture of NiO.

3.1. Ni1− xCo xCr2O4 with x ≤ 0.02

A significant drop down of the first phase transition temperature occurs when substituting even small amount of the cobalt ions [35]. The structure of the solid solutions at room temperature is cubic when x > 0.005. The second transition temperature is almost unchanged, for the crystals with small amount of substituted ions (0 ≤ x ≤ 0.02), while the phase transition to the orthorhombic phase, for the compound with x=0.02, occurs at 65 K. Fig. 1 (a) shows an example of the fit of the experimental profile by the Rietveld method. Figs. 1(b, c) shows a well resolved peak splitting as a result of the phase transition between the tetragonal and orthorhombic structures. Fig. 2 shows the temperature dependence of the lattice parameters and unit cell volume in the temperature range from 5 to 350 K.

3.2. Ni1− xCo xCr2O4 with x=0.1

At variance with above compounds the one with x=0.1 undergoes a phase transition from fcc to fct structure I41/amd at T=64 K. However, the tetragonal phase in this sample has a ratio c/a < 1, unlike the compounds with smaller x where c/a > 1. Thus, there are two anti-isotrophic phases with space group I41/amd.

Rietveld refinement fits of 20 K diffraction data to the tetragonal space group I41/amd for Ni0.9Co0.1Cr2O4 is shown in Fig. 3(a). Symmetry lowering is demonstrated by the splitting of certain high symmetry diffraction peaks as shown in Fig. 3(b–c) for
The changing of lattice parameters with temperature varying is illustrated in Fig. 4 for Ni$_{0.9}$Co$_{0.1}$Cr$_2$O$_4$. The phase transitions from tetragonal to the orthorhombic phase for the sample with $x=0.1$ could not be identified, because peak splitting is very weak. The overall shape of the peaks at high angles becomes asymmetric but peaks are not resolved. It is worth noting that such structural transition is possible from the symmetry point of view. However, both presented temperature dependences show a deviation from the main trend at temperatures below 23 K.

A set of parameters derived from the Rietveld refinement procedure for all viewed phases is shown in Table 1.

### 4. Discussion

#### 4.1. Phenomenological model

In order to describe qualitatively the thermodynamic behavior of a system, the free energy is sufficient to be present as follows:

$$
\Phi(P, T, \rho, \phi) = \Phi_0 + \alpha_1 l_1 + \beta_1 l_2
$$

$$
+ \alpha_2 l_1^2 + \beta_2 l_2^2 + \delta_1 l_2,
$$

where are two polynomial invariants:

$$
l_1 = n_1^2 + n_2^2, \quad (2)
$$

$$
l_2 = n_1^3 - 3n_1 n_2^2, \quad (3)
$$

The model based on the order-parameter expansion (1) has
been comprehensively discussed in Refs. [36–38]. The symmetrized combinations of the diagonal components of the strain tensor can be considered as OP components $\eta_1$ and $\eta_2$ for observed proper ferroelastic transformations:

$$
\eta_1 = \frac{1}{\sqrt{6}} (2\varepsilon_1 - \varepsilon_2 - \varepsilon_3),
$$

$$
\eta_2 = \frac{1}{\sqrt{2}} (\varepsilon_1 - \varepsilon_2).
$$

The experimentally measured strain can be found as

$$
\varepsilon_i = \frac{a_i}{a_0} - 1, \quad i = 1 \ldots 3,
$$

where $a_i$ – lattice parameters $a$, $b$, $c$ in pseudocubic representation; $a_0 = \sqrt[4]{abc}$ for the given temperature.

The equations of state result from the minimization of $\Phi$ with respect to the combinations of variables $\eta_i$.

The corresponding equations of state yield four possible equilibrium states:

1. $\eta_1 = \eta_2 = 0$ ($\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = 0$, $Fd3m$, parent high-temperature phase);
2. $\eta_1 = \eta_2 = \sqrt{2} \eta_3$, $I4_1/ami$ with $c/a > 1$;
3. $\eta_1 = \sqrt{2} \eta_2 = \eta_3$, $I4_1/ami$ with $c/a < 1$;
4. $\eta_1 \neq \eta_2 \neq \eta_3$, $Fd3m$.

The model-free solutions 0–III are obtained solely from the analysis of the symmetry of the parent cubic phase. Hypothesis about the microscopic mechanism of the transitions were not been used, but the theory describes all experimentally observed phase. The versatility of this approach illustrates a similar situation in a completely different chemical systems of indium alloys [39].

4.2. Symmetry mode analysis

The structure distortions in low symmetry phases can be decomposed into contributions of different collective atomic shifts with symmetries defined by irreducible representations of the parent space group. It allows to distinguishing primary and secondary (induced) contributions with different symmetries. They contribute with various weights to the whole structure distortion. The symmetry-breaking strain in a displacive phase transition is mainly induced by the freezing of the primary phonon mode, related to the order parameter, and it is the basis of their treatment within the Landau theory.

The decomposition and estimation of the amplitudes for the symmetry frozen collective atomic shifts in distortion due to displacive phase transition is a main objective of symmetry-mode analysis.

Three parameters are essential to point out a certain distortion symmetry unambiguously: a k-point, an irreducible representation (IR) and its order-parameter directions (OPD). Each distinct OPD vector will correspond to a different distortion.

We carried out decomposition and symmetry-mode analysis of the distortions using the online program ISODISPLACE [40]. Transformation matrix for tetragonal $I4_1/amd$ spinel structure from the parent cubic $Fd3m$ phase can be represented as (1/2, 1/2, 0), (1/2, 1/2, 0), (0, 0, 1) with origin shift (3/4, 3/4, 0). For the cubic to orthorhombic structural transition: (1, 1, 0), (-1, 1, 0), (0, 1, 0), (0, 0, 1), with origin shift (0, -3/2, 1/2). Results of the symmetry mode analysis are summarized in Table 2. Hereafter we use numbering of IRs and the corresponding reciprocal space vectors according to Kovalyev's tables [41]. Also Miller and Love notation [42] is specified in parenthesis, because it is used in ISODISPLACE software. Fig. 5 graphically presents primary and secondary distortion modes for NiCr$_2$O$_4$ structure.

As one can see from Table 2, the active K-vector is $k_{31}(0,0,0)$ for all transitions, which corresponds to the $I$-point at the Brillouin zone center. The spontaneous strain is associated with the $I$-point and, in the case of a proper ferroelastic transition, it is a primary order parameter. Total structure deformation consists of two components:

$$
\varepsilon_{tot} = \varepsilon_{mag} + \varepsilon_{str},
$$

where non-symmetry breaking $\varepsilon_{mag}$ corresponds to the usual thermal expansion or contraction, and does not lead to structural phase transitions, and the second, critical symmetry breaking $\varepsilon_{str}$ component is associated with the OP. The amplitudes of modes for transitions between the cubic and tetragonal phases in Ni$_{0.9}$Co$_{0.1}$Cr$_2$O$_4$ and NiCr$_2$O$_4$ have comparable magnitudes, and wherein the spontaneous deformations have the same sign, because the compression with decreasing temperature is present in all studied compounds.

### Table 1

Structural parameters of Ni$_{0.95}$Co$_{0.05}$Cr$_2$O$_4$ and Ni$_{0.9}$Co$_{0.1}$Cr$_2$O$_4$ from Rietveld refinement at various temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni$<em>{0.95}$Co$</em>{0.05}$Cr$_2$O$_4$</th>
<th>Ni$<em>{0.9}$Co$</em>{0.1}$Cr$_2$O$_4$</th>
</tr>
</thead>
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<tr>
<td>T (K)</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>Space group</td>
<td>$Fd3m$ (N227)</td>
<td>$Fd3m$ (N227)</td>
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<tr>
<td>origin</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>a (Å)</td>
<td>8.31843(8)</td>
<td>8.31843(8)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>8.31843(8)</td>
<td>8.31843(8)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>8.31843(8)</td>
<td>8.31843(8)</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
<td>575.604(17)</td>
<td>575.604(17)</td>
</tr>
<tr>
<td>Ni/Co</td>
<td>16c (0; 0; 0)</td>
<td>16c (0; 0; 0)</td>
</tr>
<tr>
<td>B$_{mag}$ (Å$^2$)</td>
<td>0.229(16)</td>
<td>0.229(16)</td>
</tr>
<tr>
<td>O</td>
<td>32e (x; x; x)</td>
<td>32e (x; x; x)</td>
</tr>
<tr>
<td>x = 0.23747(25)</td>
<td>y = 0.51629(11)</td>
<td>z = 0.23272(6)</td>
</tr>
<tr>
<td>$B_{tot}$ (Å$^2$)</td>
<td>0.554(46)</td>
<td>0.316(36)</td>
</tr>
<tr>
<td>$R_p$ (%)</td>
<td>4.91</td>
<td>4.52</td>
</tr>
</tbody>
</table>

<table>
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<tr>
<th>Crystal system</th>
<th>Cubic</th>
<th>Tetragonal</th>
<th>Orthorhombic</th>
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<td>20</td>
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<td>Space group</td>
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<tr>
<td>origin</td>
<td>2</td>
<td>2</td>
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<td>0.229(16)</td>
</tr>
<tr>
<td>O</td>
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<td>32e (x; x; x)</td>
<td>32e (x; x; x)</td>
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<td>$R_p$ (%)</td>
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<td>4.52</td>
<td>4.52</td>
</tr>
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</table>

By contrast, the amplitude of the primary modes $\tau_2(GM3 +)$ differ by two orders of magnitude: amplitude is significantly greater for concentrated JT system NiCr$_2$O$_4$ than for Ni$_{99.9}\text{Co}_{0.005}\text{Cr}_4\text{O}_4$. Moreover, the primary mode amplitude of the displacements of the oxygen atoms in the spinel NiCr$_2$O$_4$ exceeds an order of magnitude of the non-symmetry breaking temperature compression one. This fact is one of the features of concentrated JT systems: increasing the unit cell parameters along certain crystallographic directions with decreasing temperature, or applying hydrostatic pressure. The corresponding spontaneous strains have a different sign, which related to the behavior of OP predicted for two anti-isostuctural phases in the corresponding phenomenological model.

A similar situation occurs for solid solutions Ni$_{1-x}$Cu$_x$Cr$_2$O$_4$ over temperature [43,44] and hydrostatic pressure changes [45]. Although in terms of the microscopic mechanism the situation in solid solutions of nickel and copper chromites is quite simple: the competing distortions involved in the cooperative Jahn–Teller effect give rise to two anti-isostuctural phases, JT mechanism is dominant, and it completely suppresses possible effects of weak spin-orbit interaction in the structure. In solid solutions of nickel and cobalt chromites such a mechanism does not work due to the spin-orbit interaction in the structure. In solid solutions with $\text{CoCr}_2\text{O}_4$, must be higher $\text{Fddd}$ than energy lost resulted from the degeneracy appearing. Further distortions of tetrahedra and octahedra in anti-isostructural tetragonal phases with two indexes, which are both dimensionless and independent on size of polyhedron. The distortion index and quadratic elongation calculated as follows [46,47]

$$D = \frac{1}{n} \sum_{i=1}^{n} \frac{l_i - l_{av}}{l_{av}},$$

$$(\lambda) = \frac{1}{n} \sum_{i=1}^{n} \left( \frac{l_i}{l_0} \right)^2,$$

where $D$ is a distortion index, $l_i$ is the distance from central atom to $ith$ coordinating atom, $l_{av}$ is the average bond length, $(\lambda)$ is quadratic elongation, $l_0$ is the center-to-vertex distance of a regular polyhedron of the same volume. For regular polyhedra in cubic phases the distortion index is 0 and quadratic elongation is 1.

From Table 3 it is clear that the distortions of the tetrahedra are negligible for tetragonal phase of Ni$_{100}\text{Co}_{0.005}\text{Cr}_4\text{O}_4$, whereas the distortion index of octahedra is three times higher than in the first sample with $c/a > 1$. That is strong evidence of the primary role playing by the oxygen octahedra distortion in the formation of the tetragonal phase with $c/a < 1$. The IR $E_g$ enters to the composition of a mechanical representation on Wyckoff positions $32(e)$ and octahedral tilt representation [48]. Therefore the chain of structural transitions $\text{Fd3m} \leftrightarrow 4\text{I}4\text{am} \leftrightarrow 4\text{Fdd}$ of the displacement type connected with octahedral tilt. For these reasons low-symmetry $4\text{I}4\text{am}$ and $4\text{Fdd}$ phases formed by octahedra tilting in the spinel structure [48].  

Note the structural features of the tetragonal and orthorhombic structures of deformed spinel induced by rotation of the octahedral: the ordered arrangement of elongated (shortened) octahedra is not a “pure” ordering of the “ferro” type. The axes of elongated (shortened) octahedra and tetrahedra are parallel to each other in the case of “ferro”-type ordering (similar to parallel orientation of magnetic moments in ferromagnetics). The tilting of the octahedra leads to deviation from a parallel orientation of elongated (shortened) octahedral, more complex structure.

5. Conclusion and overview

The unified phenomenological theory predicts for Ni$_{1-x}$Cu$_x$Cr$_2$O$_4$ solid solutions all the structural phases experimentally observed so far. The corresponding model justifies the anomalous elastic anisotropy by relating it to the spontaneous strain induced by a proper ferroelastic transition. However, the
microscopic origin of the appearance of tetragonal phase is difficult to specify, because simultaneous acting of several mechanisms associated with different types of exchange and spin-orbital ordering is possible. However, when looking for a microscopic mechanism of the macroscopic elastic instability one should rely on the symmetry of the order parameter as a selection rule. We investigated the structure of solid solutions with mixed JT and non-JT ions in tetrahedral positions, which show unusual structural phase transitions. Certainly, the microscopic mechanism forming the new tetragonal phase cannot be determined solely on the basis of X-ray diffraction studies. Therefore, we call for additional works on neutron diffraction and magnetization measurements in order to determine the magnetic structure of solid solutions, and, for clarify, the role of magnetic ordering in the formation of the tetragonal phase. Also the calorimetric measurements are needed as an independent determination of the temperatures of the magnetic and structural transitions, and their origin.

Acknowledgements

The authors acknowledge SLS for granting the beamtime. We thank as well SNBL for the opportunity of performing a part of synchrotron experiments. The research was partially supported by the Russian Foundation for Basic Research (Grant no. 13–02–12416 of m2). Some results of this work have been obtained with the support of the Ministry of Education and Science of the Russian Federation in the framework of the State task (Talanov V.M., project N2983/9.14).

References


Fig. 5. The distortions corresponding to the IR \((\eta, \xi, \gamma)\) GM3 \(\epsilon\) (a) projected along the \([0.5 1 0]\) direction with \([0 0 1]\) upward vector; \((\xi, \eta, \gamma)\) GM3 \((b)\) projected along the \([0.2 1 0]\) direction with \([0 0 1]\) upward vector; GM1 \((c)\) projected along the \([0.2 1 0]\) direction with \([0 0 1]\) upward vector, and for tetragonal to orthorhombic transitions \((d)\) projected along the \([1 1 0]\) direction with \([0 0 1]\) upward vector, in NiCr2O4. Ni and Co (blue) are tetrahedrally coordinated by oxygen (red). Chromium atoms are shown in green. The scale of the displacement vectors is arbitrary. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

Fig. 6. Splitting of d energy levels for Ni\(^{2+}\) in regular tetrahedral surrounding of ligands with fully occupied \(e_g\) orbitals and partially occupied of \(t_{2g}\) orbitals (JT active case). Orbital splitting in the cases of further deformation are shown.

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>(D_{tet})</th>
<th>(\langle\lambda\rangle_{tet})</th>
<th>(D_{oct})</th>
<th>(\langle\lambda\rangle_{oct})</th>
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<td>1.0053</td>
<td>0.00026</td>
<td>1.0092</td>
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<td>0</td>
<td>1</td>
<td>0.00078</td>
<td>1.0095</td>
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