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Structural and magnetic properties of Cu–Ni–Cr spinel oxides

M. Tovar[a,*], R. Torabi[a], C. Welker[b], F. Fleischer[c]

[a]Hahn-Meitner-Institut Berlin, Glienicker Str. 100, D-14109 Berlin, Germany
[b]University of Cape Town, South Africa
[c]Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany

Abstract

The compounds $CuCr_2O_4$ and $NiCr_2O_4$ crystallize at room temperature in a tetragonal distorted spinel structure, s.g. $I4_1/amd$, with axes ratio $c/a<1$ and >1, respectively. The distortion is caused by the Jahn–Teller ions Cu^{2+} and Ni^{2+} which flatten or elongate their surrounding oxygen tetrahedron. $CuCr_2O_4$ and $NiCr_2O_4$ form a complete solid solution series $Cu_{1-x}Ni_xCr_2O_4$ where for $0.825<x<0.875$ members with orthorhombic symmetry were found. Using neutron powder diffraction and thermal analysis methods several members of the solid solution series were investigated. On cooling, all samples showed a temperature-dependent crystallographic phase transition from cubic to tetragonal symmetry between 865 K ($CuCr_2O_4$) and 310 K ($NiCr_2O_4$). The phase $Cu_{0.15}Ni_{0.85}Cr_2O_4$ undergoes a second crystallographic transition to orthorhombic symmetry, space group Fddd, at $T=300$ K. The neutron diffraction experiments as well as SQUID measurements reveal magnetic ordering of the ions between 150 and 50 K which partially occurs as a two-step mechanism.

Keywords: Jahn–Teller; Rietveld analysis; Spinel; Phase transition; Magnetism

1. Theoretical background

Oxide systems are well suitable systems for systematic studies of macroscopic and microscopic structure distortions due to the Jahn–Teller effect. The Jahn–Teller effect means that an ion being in an energetic degenerated ground state (which holds for several transition metal ions) reduces its local symmetry to overcome the degeneration. The direction of the distortion can partially be predicted using orbital schematic considerations [2]. For example the introduction of Cu^{2+} ion (d^9 system) in a tetrahedral (oxygen) environment leads to a flattening of the tetrahedron, while the tetrahedron is elongated in case of Ni^{2+} (d^8 system) (Fig. 1) [1,3].

Thus introducing Cu^{2+} or Ni^{2+} into the tetrahedral site of a cubic chromium spinel ($[T^{2+}]Cr_2O_4$) leads to strong local tetrahedral distortion which further causes a macroscopic and temperature-dependent distortion of the cubic spinel structure. Since the direction of the structure distortion caused by these two ions are oppositional, in the solid solution series $Cu_{1-x}Ni_xCr_2O_4$ several interesting crystallographic phenomena can be observed which are topic of this work.

2. Experimental

Synthesis of the samples was done by precursor method where the educts Cu(II) acetate, Ni(II) acetate and Cr(III) nitrate were mixed in the appropriate amounts. Urea was added to support complete combustion of the educts. The resulting nanosized powder was annealed for 24 h at 1100 K to give the desired product.

It turned out that the synthesis of pure samples became more difficult with increasing Ni content. Thus, samples with $x>0.6$, even after longer annealing time still showed some impurities of Cr_2O_3 which was taken into Rietveld calculations as an additional phase. However, samples with $x=0$, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.85 could be synthesized as pure phases, no significant additional reflections could be detected in the X-ray diffractograms.

Using differential scanning calorimetry (DSC) as well as low-temperature X-ray diffraction (Guinier method) all

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*Corresponding author. Tel.: +49 30 8062 2768.
E-mail address: tovar@hmi.de (M. Tovar).

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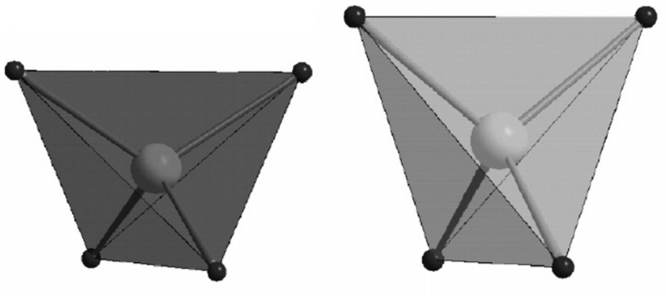

(a) Flattening of CuO_4 tetrahedron (b) Elongation of NiO_4 tetrahedron

Fig. 1. Jahn–Teller effect on CuO_4 and NiO_4 tetrahedron.

samples were investigated for crystallographic phase transitions. To avoid high and irregular background due to incoherent scattering of Cr^{3+} and Ni^{2+} ions when exposed to Cu-anode X-rays and in order to investigate the complete required temperature range with high precision and low thermal gradient, all crystallographic information were extracted from neutron powder diffraction data collected at the E9 neutron powder diffractometer at BENSC, HMI, Berlin. Additional magnetic information were gained by SQUID magnetometry.

3. Results and discussion

The phase diagram was established and revised since only incomplete or theoretical data could be found in the literature. DSC as well as low-temperature X-ray and neutron diffraction experiments revealed three different phase regions: cubic, tetragonal and orthorhombic (Fig. 2).

As can be seen, the experimentally determined phase boundary between the tetragonal and the orthorhombic phase deviates notedly from the reported calculated curve [4] (dashed lines in Fig. 2). All samples with $x<0.7$ and >0.9 exhibit tetragonal symmetry down to 2 K, only samples with $x=0.8$, 0.85 and 0.9 showed orthorhombic symmetry on cooling below room temperature. Thus the orthorhombic region is much smaller than was expected.

Room temperature neutron powder diffraction data (Fig. 3) were used for Rietveld analysis of the crystal structures. In the picture a crossover of the reflection at sample $x=0.85$ is marked. This crossing is due to changing of the c/a ratio of the tetragonal spinels. While due to Jahn–Teller *flattening* $CuCr_2O_4$ shows axes ratio $c/a<1$, $NiCr_2O_4$ shows $c/a>1$ due to Jahn–Teller *elongation*. The crossing point is close to the end member $NiCr_2O_4$ since the Jahn–Teller effect for Ni^{2+} is much weaker than for Cu^{2+}. The observations are in good agreement with further investigations.

The influence of the Jahn–Teller effect on the individual tetrahedra can be better seen and estimated by looking to the inner dimensions of the tetrahedra. In Fig. 4 distances Cu/Ni–O and angles O–Cu/Ni–O are plotted as function of composition. In a flattened tetrahedron (CuO_4) there are—in respect to the ideal tetrahedron angle 109.4°—four smaller angles and two larger ones, while in an elongated

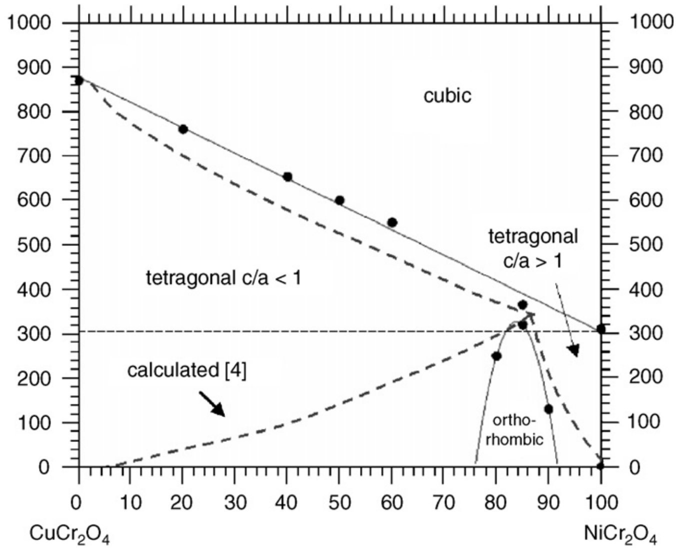

Fig. 2. Phase diagram of the system $CuCr_2O_4$–$NiCr_2O_4$.

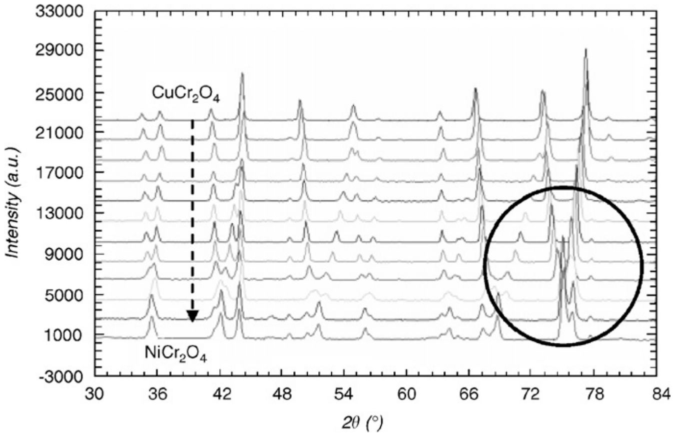

Fig. 3. Neutron powder diffractograms of the members of the solid solution series $Cu_{1-x}Ni_xCr_2O_4$.

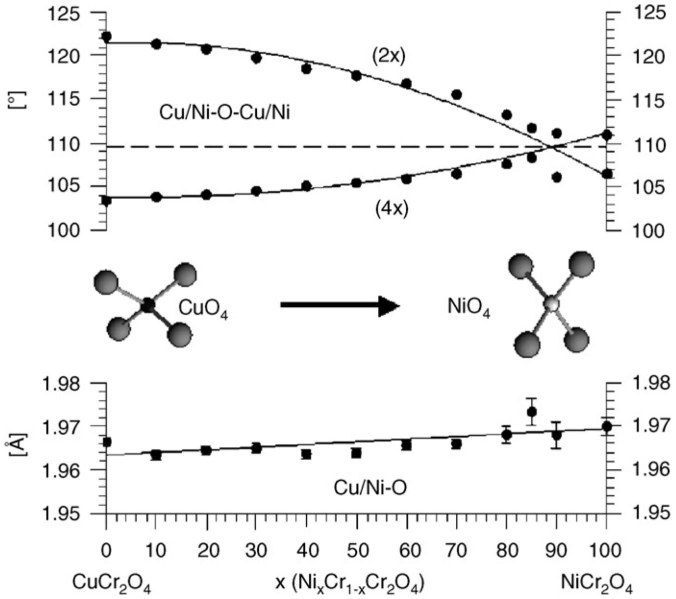

Fig. 4. Bond distances and angles in the Cu/NiO_4 tetrahedra.

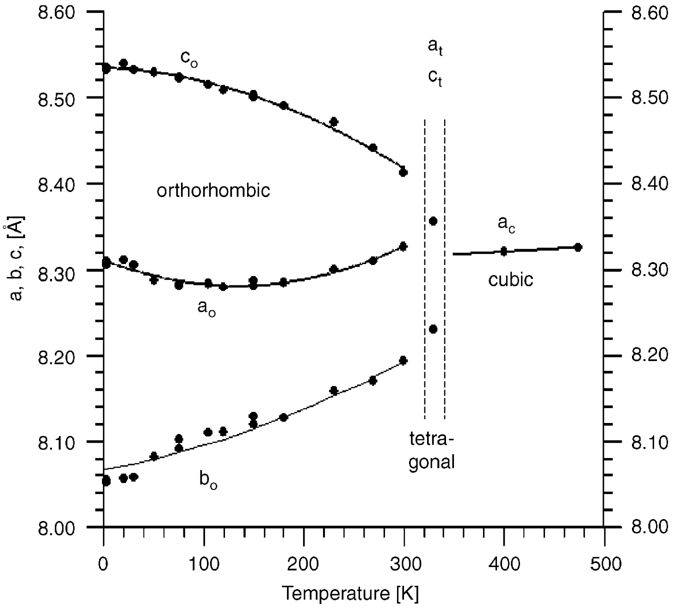

Fig. 5. Lattice parameters of $Cu_{0.15}Ni_{0.85}Cr_2O_4$ as function of temperature.

tetrahedron (NiO_4) it is vice versa. Hence obviously not only the lattice parameters crossover but also the inner tetrahedral angles. They start for CuO_4 at 104.5 ° (4x) and 122.0 ° (2x) and end for NiO_4 at 111.0 ° (4x) and 106.5 ° (2x) while the distances Cu/Ni–O remain quite constant at about 1.965 ± 0.005 Å.

As can be seen from the phase diagram (Fig. 2) the phase $Cu_{0.15}Ni_{0.85}Cr_2O_4$ undergoes two crystallographic transitions: cubic to tetragonal at 350 K and tetragonal to orthorhombic at 300 K. Temperature-dependent neutron powder diffraction was carried out to study the crystal structure as a function of temperature and to determine the still unknown low-temperature crystal structure (which has to be discussed elsewhere). From Fig. 5 it can be nicely seen that the respective phase transition is of first-order character due to jumps in the lattice parameters from the particular low-temperature to the high-temperature phase.

At temperature below 50 K all investigated samples showed magnetic ordering (see also Ref. [5]) in the neutron diffractograms. SQUID measurement revealed that the transition temperature strongly depends on the Cu/Ni ratio (Fig. 6) and that the transition of $Cu_{0.15}Ni_{0.85}Cr_2O_4$ occurs in two steps. Additional neutron powder diffraction investigations with finer temperature intervals confirmed this observation.

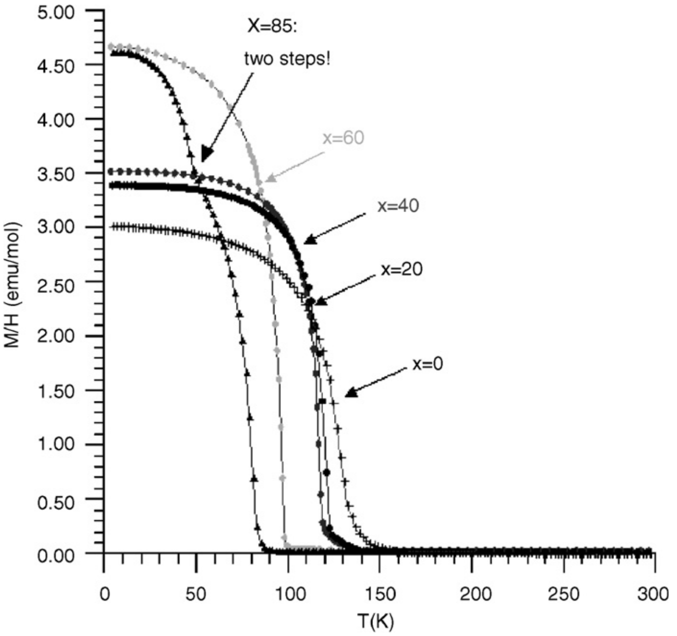

Fig. 6. SQUID measurements of the members of the solid solution series $Cu_{1-x}Ni_xCr_2O_4$.

4. Conclusion

The system $Cu_{1-x}Ni_xCr_2O_4$ is strongly influenced by the Jahn–Teller effect which gives rise to symmetry reduction from cubic to tetragonally and orthogonally distorted spinel structure. The latter shows highly anisotropic thermal expansion which can be ascribed to the oppositional behaviour of Cu^{2+} and Ni^{2+}.

At low temperatures all compounds show anti-ferromagnetic ordering. T_N decreases and the magnetisation increases with increasing Ni content. This corresponds to the fact that Ni^{2+} has two unpaired electrons whereas Cu^{2+} has only one. The observed two-step mechanism may have its origin in different ordering temperature of the ion's sublattices.

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