

THE PHYSICAL PROPERTIES OF SOME MIXED CHLORIDES WITH THE SPINEL STRUCTURE

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This paper present the first investigation results of the not previously investigated mixed chlorides of transition metal of a general formula Ta_2Cl_8 , where $T=Mn, Co, Ni, Cu$. The investigation is performed using the diffuse reflectance spectrophotometry and the measurement of the magnetic susceptibility.

INTRODUCTION

The physical properties of the different mixed chlorides containing transition metal ions (T) are been subject of many studies (e.g./1,2/). These mixed chlorides, mainly with the alkaline metal ions have the chemical composition and crystal structures of the corresponding oxides. It is interesting that the spinel type chlorides are not investigated, although the investigation of the phase diagrams of certain binary systems, including T-Al chlorides, show the existence of the such compounds (e.g./3,4/). Further, the crystal structure investigation of the $CoAl_2Cl_8$ shows that this compound has the spinel structure /5/.

In this paper the first results of the investigations of the four mixed chlorides of a formula TAl_2Cl_8 , where $T = Mn, Co, Ni, Cu$ are investigated. The investigations include the synthesis, the crystallographic examination and the first studies of the certain physical properties.

EXPERIMENTAL

The synthesis of the TCl_2Cl_8 compounds is accomplished by mixing the corresponding transition metal chloride (n-hydrate) and $AlCl_3 \cdot 6H_2O$ in the stoichiometric proportion and heating in such a way formed mixture till a temperature determined by the corresponding T-ion. The composition of these very hygroscopic compounds is con-

trolled by the methods of the chemical analysis. The diffractograms obtained by the method of the x-ray powder diffractometry correspond to the samples of cubic symmetry, i.e. that the examined compounds have spinel structure, although the diffractogram of CuAl_2Cl_8 demands a supplementary investigation of this compound.

The synthesized compounds are examined by the method of the diffuse reflectance spectrophotometry. The corresponding spectra in the Fig. 1. are shown. The measurements of the magnetic susceptibilities are carried out also. The susceptibilities are measured by the force method in the magnetic field with the maximal induction $B = 0,6$ T. These measurement are performed in the temperature range from 120 to 300 K.

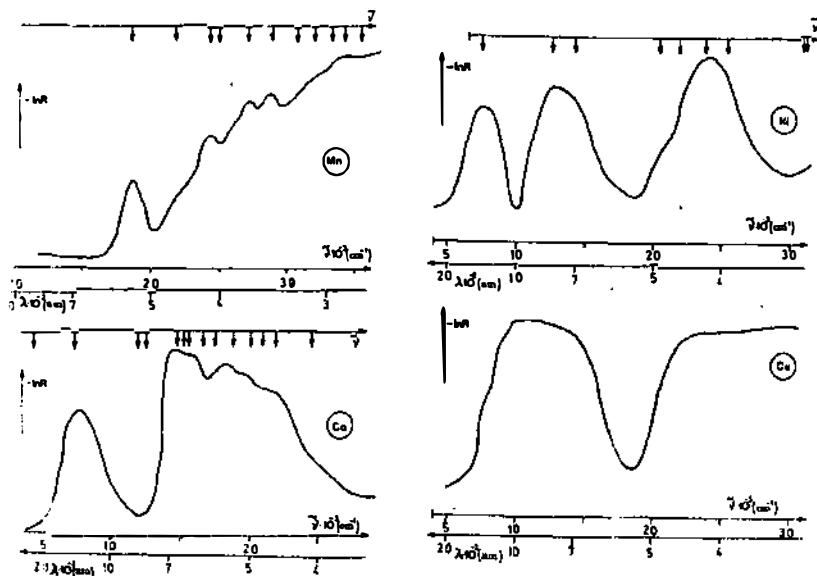


Fig. 1. The optical reflection spectra of the TAl_2Cl_8 compounds

RESULTS AND DISCUSSION

The first examination of the recorded spectra shows by comparison (e.g./6/):

1. The spectra of the Mn(II) and Ni(II) compounds correspond to the crystal field spectra of these ions in the octahedral surrounding.

2. The spectrum of the Co(II) compound corresponds to the crystal field spectrum of this ion in the tetrahedral surrounding (or predominantly in the tetrahedral surrounding).

3. The CuAl_2Cl_8 spectrum consists of one band characteristic for the d^1 ion. This broad band centred at about 11000 cm^{-1} is the result of the superposition of a few narrower bands which correspond to the electronic transitions of d^1 ions in the octahedral crystal field with a certain tetragonal or trigonal distortion. The high frequency part of the spectrum which lies at the wave numbers $\tilde{\nu} > 22000\text{ cm}^{-1}$ represents the charge transfer spectrum /7/.

The Mn(II), Ni(II) and Co(II) spectra re interpreted by the use of the method given in /8/. The determined corresponding electronic transition are marked in Fig. 1. by the arrows. This interpretation enables the evaluation of the crystal field parameters of the corresponding ions (Table 1.).

It is interesting that the optical spectrum shows that the Co(II) ions are distributed completely or almost completely in the tetrahedral holes of the spinel structure. This is a result which give also the spectroscopic investigations of the oxide spinels (e.g. /9,10/), but it is in a disagreement with the standard references dedicated to the ferrite materials (e.g./11/).

The magnetic measurements show that the investigated spinels with one magnetic sublattice in the examined temperature range are Curie-Weiss paramagnets. The experimental values of the magnetic susceptibility after correction for the diamagnetic contribution /12/ enable the claculation of the magnetic moments (μ) of the T(II) ions. This procedure gives

$$\mu(\text{Mn}) = 5,87\mu_B,$$

$$\mu(\text{Ni}) = 3,83\mu_B,$$

$$\mu(\text{Co}) = 3,98\mu_B,$$

$$\mu(\text{Cu}) = 1,71\mu_B,$$

(μ_B = Bohr magneton).

Table 1. The crystal field parameters for the chloride spinels

PARAMETER	Octahedrally coordinated ions		Tetrahedrally coordinated ion
	Mn	Ni	Co
10 Dq	7400 cm ⁻¹	7700 cm ⁻¹	4200 cm ⁻¹
B	784 cm ⁻¹	882 cm ⁻¹	740 cm ⁻¹
β	0,86	0,86	0,73

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