

OPTICAL, MAGNETIC AND DIELECTRIC PROPERTIES OF
Co(II) AND Ni(II) ARSENATE WITH VIVIANITE STRUCTURE
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INTRODUCTION

According to literature data /1/, the compounds $\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ (erythrin mineral) and $\text{Ni}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ (annabergit mineral) are isostructural between each other and with the appropriate two phosphates, as well as with $\text{Fe}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ (parasymplesit) and $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (vivianite). Determination of crystalline structure of these compounds /2,3/ has shown that the crystals possess monoclinic symmetry and that M(II)-ions in this structure could be found in two different coordination surroundings formed by oxygen atoms from XO_4^{3-} ions (X=P or As) and from H_2O molecules.

The paper cover investigation results of the compounds $\text{M}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ where M=Co and Ni; researches have been made on polycrystalline samples synthesized in our laboratory by the method described in /4/. It is, in fact, continuation of an earlier work on isostructural phosphates /5/.

OPTICAL SPECTRA

By applying the method of diffuse reflectance spectroscopy, the spectra of Co(II) and Ni(II) arsenate are obtained within the range of 357nm+2500nm (i.e. $2,8 \cdot 10^4 \text{cm}^{-1} + 4 \cdot 10^3 \text{cm}^{-1}$). Spectroscopy is realised at a room temperature in relation to BaSO_4 as reference sample. The spectra recorded are shown in Fig.1. The spectra are represented by two lines: full line showing the relative reflectance and dotted line showing so-called Kubelka-Munk function /6/. Comparison shows identical peak patterns.

Analysis of these spectra is realised on the assumption on the existence of a "mean" octahedral surrounding for M(II)-ions in crystals. Such an approach has been adopted because the wide spectral bands originating from two different crystal (ligand) field spectra overlap and because deformations of these octahedral surroundings are small, so that it is rather difficult to give a reliable interpretation which would take into consideration the different deformations /7/. It is also important that error in interpretation of spectrum depends on the difference in numbers of reliably determined spectral transitions and of crystal field parameters /8/; assumption of a mean octahedral field means introduction of the minimal number of parameters.

The first spectrum analysis has been made with applications of König-Kremer's diagrams /9/; attention had to be paid here to the fact that the reduction of crystal field symmetry partially eliminated degeneration of T-level ($i \neq 10, 11$) which is particularly noticeable within the range of 7000 cm^{-1} . With application of the appropriate relations /10, 11/ numerical evaluation of the positions of the spectral band and calculations of crystal parameters have been carried out. The spectra analysis results are shown by arrows in Fig. 1. and the parameter calculated are given in Table 1.

Table 1.

COMPOUND	CRYSTAL FIELD PARAMETERS		
	$10Dq (\text{cm}^{-1})$	$B (\text{cm}^{-1})$	$\beta = B/B_0$
Co(II)arsenate	8480	823	0,86
Ni(II)arsenate	8520	906	0,87

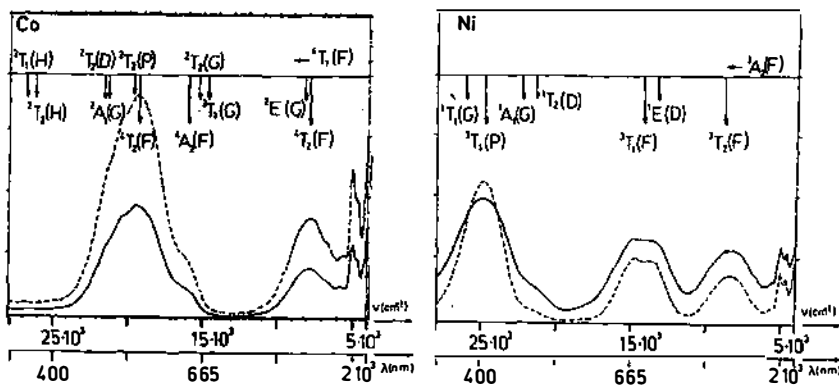


Fig. 1.

MAGNETIC AND DIELECTRIC MEASUREMENTS

Within the temperature range of $100 + 300\text{K}$ temperature dependence has been studied of

- Magnetic (mass) susceptibility (χ_m) measured by Gouy method; measuring results are given in Fig. 2;
- Dielectric (relative) permittivity (ϵ_r) measured: b.1. by high-frequency measuring bridge (at 1 MHz) and b.2. by resonant measuring unit (at 800 Hz); the results of measurements are respectively shown in Fig. 3. and 4;
- Dielectric losses ($\text{tg } \delta$) at 800 Hz; the measuring results are shown in Fig. 5.

Measurements under b. and c. are made on pellets of powder pressed at 5 MPa. Shortly, dependences $1/\chi_m$ and ϵ_r on temperature (T) have forms characteristic for paramagnets and linear dielectrics; this also applies to Fig. 5. But the lines in Fig. 3 + 5. have discontinuities which correspond to change in functional dependence. These discontinuities correspond to various

structural phase transitions in the compounds investigated. The mean temperatures of three phase transitions for Co-arsenate equals to 135K, 191K, and 245K and for Ni-arsenate 129K, 197K and 248K.

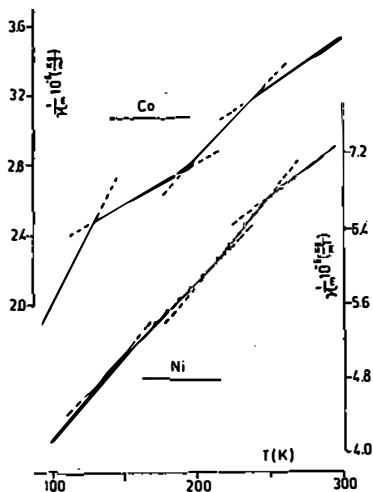


Fig. 2.

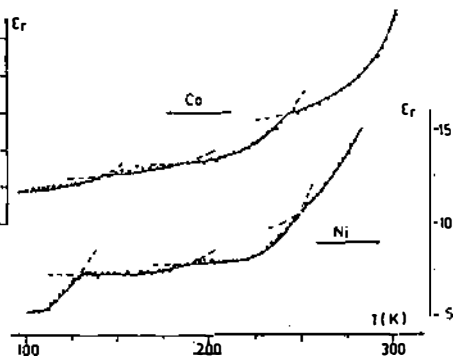


Fig.3.

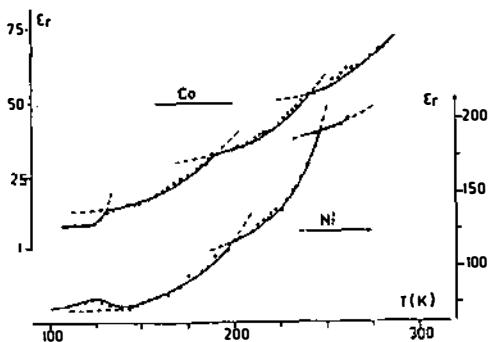


Fig.4.

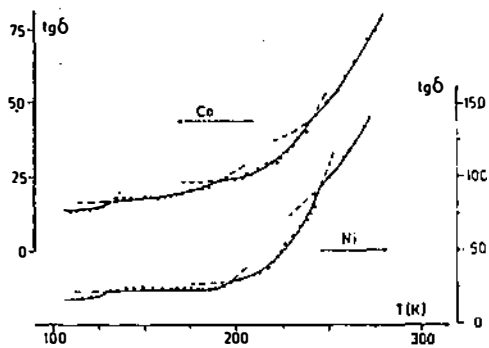


Fig.5.

CONCLUSION

Crystal field spectra of Co(II) and Ni(II)-compounds have been studied and found out that the crystal field strength ($10Dq$) is higher for Ni(II) compound; the same fact has been established for a series of phosphate and aquo-complex compounds /5,12/. In the temperature range of 100 + 300K, three structural phase transitions have been established; the analogous result has been found in isostructural phosphates /5/. Similar phenomenon has been discovered and studied for a long time in perchlorate - hydrates (f.e./13,14/).

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