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INVESTIGATION OF PHYSICAL PROPERTIES OF $K_3[Fe(NCS)_6].4H_2O$

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A complex investigation of $K_3[Fe(SCN)_6].4H_2O$ was performed by means of plotting the optical reflection spectrum and measuring magnetic susceptibility and dielectric permittivity. Dehydration temperature was determined on the basis of DTA thermogram, which enabled us to obtain and investigate of the anhydrous product.

INTRODUCTION

Complex thiocyanates of transition metals have so far been very few investigated. Literature that deals with these substances is very scarse /1,2/. The crystal structures of the tetrathiocyanate complex compound $K_2[Co(NCS)_4].4H_2O$, is known as well as hexathiocyanate complex compounds $K_3[Cr(NCS)_4].4H_2O$ and $K_4[Ni(NCS)_6].4H_2O$ /2/. The optical absorption spectra of some complex compounds in the solution /1,3/, including also the spectrum of $[Fe(NCS)_6]^{3-}$-ion /3/, have already been investigated. We could not find other data on these substances.

In this paper are presented data on the investigation of Fe^{3+} complex thiocyanate. These are the first results obtained in the investigation performed on the polycrystalline material.

EXPERIMENT

By means of a simple procedure based on the reaction of sedimentation /1/, a polycrystalline substance was obtained from the solution which had prior to that been kept still for several days, and was identified by thermogravimetric analysis as $K_3[Fe(NCS)_6].4H_2O$. DTA thermograpm plotting has shown that the substance dehydrates at the temperature below 100°C, while the desintegration of the anhydrous substance starts at 250°C. The dehydration was performed by heating the substance at the temperature about 100-110°C and the anhydrous substance $K_3[Fe(NCS)_6]$ was obtained.

Diffractogram plotting was performed by the x - ray diffractometric method. This diffractogram does neither provides a reliable determination of the crystal lattice symmetry of this substance nor the determination of the unit cell. However, a comparison of the hydrated and anhydrous substance diffractograms offers interesting information, i.e. that the crystal structure does not change with anhydration. Taking into consideration the known hexathiocyanate structures, we can draw a conclusion that the molecules of the water are placed into the lattice holes formed by $[Fe(NCS)_6]^{3-}$ octahedrons and K^+-ions in a way similar to that of the somewhat different complex compounds - complex cyanates of iron /4/.

The polycrystalline samples obtained were investigated by means of the optical reflection spectrophotometry method in the range between 360 and 950 nm. The magnetic susceptibility was measured by Faraday method and the dielectric permittivity was determined by the resonant method at 800Hz.

MEASUREMENT RESULTS

Magnetic susceptibility measurement has enabled determination of the magnetic moment of Fe^{3+}-ion in this substance. The value of the effective magnetic moment of Fe^{3+} ion in $K_3[Fe(NCS)_6]$. $4H_2O$ is M_{eff} = = $2,6\mu_B$, while it is $2,15\mu_B$ in $K_3[Fe(NCS)_6]$. These values can hardly be explained by the theory of weak or strong crystal field /5/ only; the effect of the medium strong crystal field is very probably in question.

This conclusion seem to be proved by the optical spectra plotted (2). Fig. 1. shows dependence of the relative reflectance measured taking $BaSO_4$ as a standard, on the wave number $^1/\lambda$. The figure shows three spectra: tetrahydrate spectrum (1), the anhydrous substance spectrum (2), and $K_3[Fe(CN)_6]$ spectrum (3). Somparison shows that when passing from the spectrum(1). to the spectrum(3).there is a shift, in wave numbers of observed band, accompanied with the appropriate "deformation", toward higher energies, what means that the crystal field intensity increases from the substance(1). toward the substance(3).

The informations offered by spectra 1. and 2. are too scarce for a successful interpretation. However, they indicate that it would be interesting to plot spectra in a significantly broader spectrum interval; these spectra, plotted at lower temperature, could serve as a starting point for the interpretation of Fe^{3+}-ion spectrum in the stronger crystal field, because the interpretations so far obtained are not sufficiently reliable /6/.

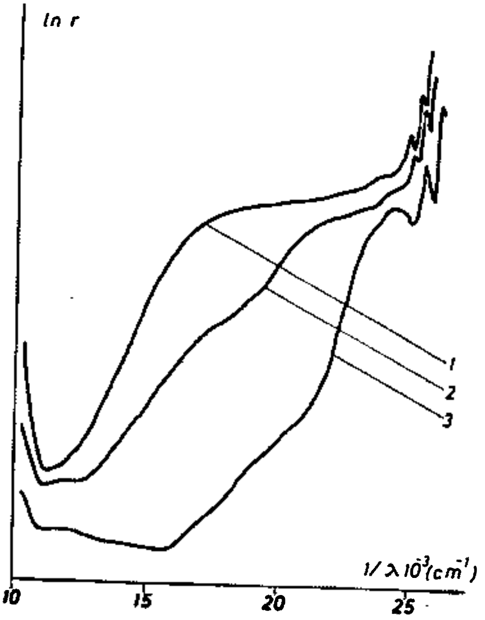

Fig. 1. Reflectance spectra of : 1.$K_3[Fe(NCS)_6].4H_2O$, 2. $K_3[Fe(NCS)_6]$, 3. $K_3[Fe(CN)_6]$.

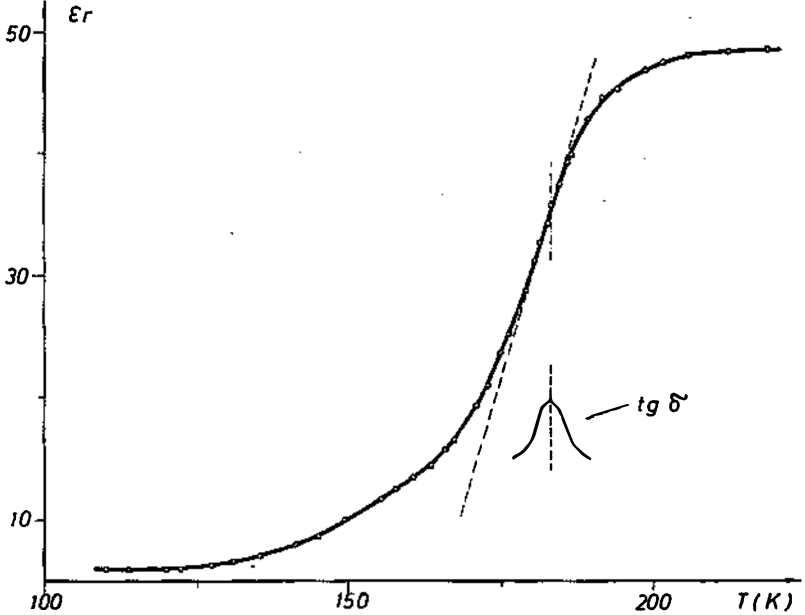

Fig. 2. Dielectric permittivity $\epsilon_r(T)$.

Fig. 2. shows the variation of the relative dielectric permittivity ε_r for $K_3[Fe(CN)_6].4H_2O$ on temperature, measured at 800 Hz in the temperature interval from 100 to 200K. A characteristic increase is noticed with transition through the inflection point. The inflection point on the curve corresponds to the maximum of losses ($tg\delta$). Such behaviour of ε_r points out the possibility that there is a phase transition of the so far undetermined nature in this substance.

CONCLUSION

The synthetized substance $K_3[Fe(CN)_6].4H_2O$ shows interesting features that demand a more detailed investigation. Further investigations, and especially the determination of the crystal structure and investigation of the function $\varepsilon_r(T)$ shall be performed on monocrystals in the near future.

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