Thermochimica Acta, 92 (1985) 823-826
Elsevier Science Publishers B.V., Amsterdam

THE DTA AND X-RAY PRELIMINARY STUDY OF Rb_2CoCl_4, Cs_2CoCl_4 AND Li_2CoCl_4

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ABSTRACT

The DTA and X-ray preliminary study of Rb_2CoCl_4, Cs_2CoCl_4 and Li_2CoCl_4 is presented. The DTA peaks correspond to the structural phase transitions. The modulated crystal phases for Rb_2CoCl_4 and Cs_2CoCl_4 were found.

INTRODUCTION

The transition points in $/NH_4/_2ZnCl_4$ found by two of us[1] with the aid of DTA, namely: ~263k, ~323K, ~393K, as well as the chemical decomposition point equal ~423K have been confirmed by the other authors[2,3] as being connected with the electrical phase transitions These transition points were - with exclusion of 323K - also confirmed by the X-ray diffraction study[4,5]. Therefore, a preliminary study of similar compounds, i.e. Rb_2CoCl_4, Cs_2CoCl_4 and Li_2CoCl_4, is presented.

EXPERIMENTAL

The obtained compounds as well as the substrata are highly higroscopic, therefore all the operations were carried out in a glove-box in the atmosphere of either dry argon or nitrogen. The substrata were dehydrated by heating the quartz ampules connected with a vacuum pump. Then the substrata were weighed in a glove-box in the stoichiometric relation and placed in an ampule, which was pumped out down to vacuum of $\sim 10^{-1}$P and sealed. After having mixed the substrata in the ampules, the latter were placed in a resistance furnace and heated up to the melting points of these compounds. After melting the substance in a quartz ampule the furnace temperature was lowered of about 100K and the compounds were heated up during about 2 weeks. Then the ampules were opened in a glove-box and the compounds were prepared to further investigations. In this way the compounds Rb_2CoCl_4, Cs_2CoCl_4 and Li_2CoCl_4

Proceedings of ICTA 85, Bratislava

were obtained. The DTA, DTG and TG /DERIVATOGRAPH Q-1500/ study was carried out for these compounds. The X-ray powder diffractometers HZG 4/A and DRON 3.0, combined with both low temperature attachment URNT-180 and high temperature attachment UWD-2000, were used. The two temperature attachments could be placed not only on the DRON 3.0 diffractometer but also on the HZG 4/A diffractometer with the aid of a special adapter developed by us.

RESULTS

The phase transition points found with the aid of DTA are presented in the table:

Compound	Temperature range, K	Phase transition, K
Rb_2CoCl_4	285 - 823	628, 685
Cs_2CoCl_4	282 - 873	618, 721
Li_2CoCl_4	288 - 873	543

With the aid of X-ray diffraction the temperature dependence of the lattice parameters for the compounds under study was determined, namely for Rb_2CoCl_4 in the temperature range 103 - 713 K /Fig. 1/ and for Cs_2CoCl_4 in the temperature range 123 - 723 K /Fig. 2/.

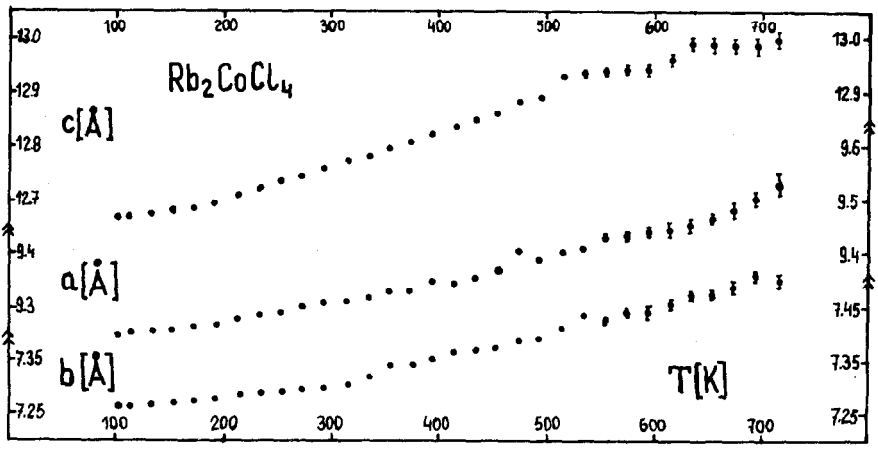

Fig. 1. Lattice parameters for Rb_2CoCl_4 vs. temperature

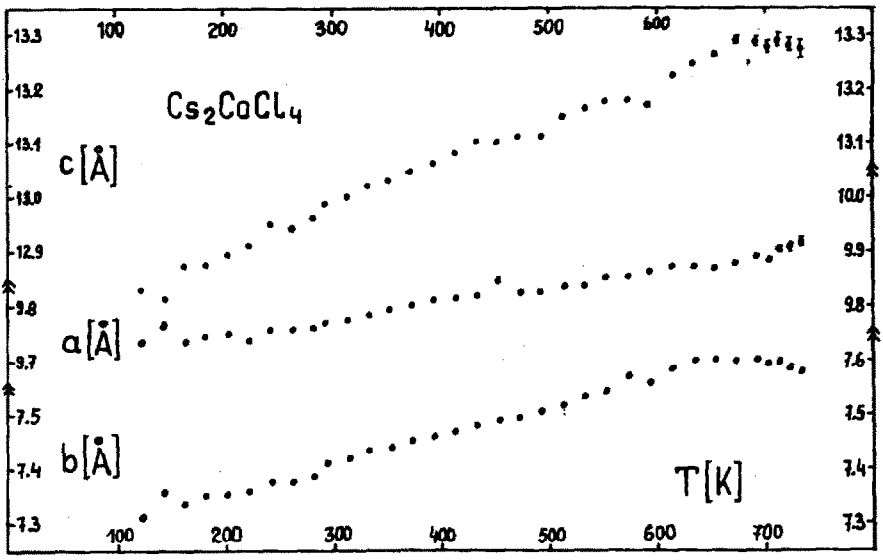

Fig. 2. Lattice parameters for Cs_2CoCl_4 vs. temperature

Above these temperatures the new phases develop for the two compounds, but they remain not identified so far. For Rb_2CoCl_4 in the temperature range 103 - 133 K and for Cs_2CoCl_4 in the temperature range 123 - 290 K the modulation of the crystal structure was observed. The modulation parameter p equal $|\vec{p^*}/\ \vec{b^*}|$ /where $\vec{p^*}$ is a modulation vector/ is presented in Figures 3 and 4.

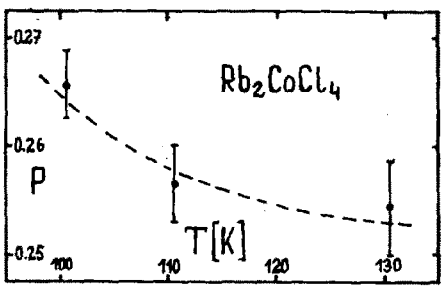

Fig. 3. Modulation parameter for Rb_2CoCl_4 vs. temperature

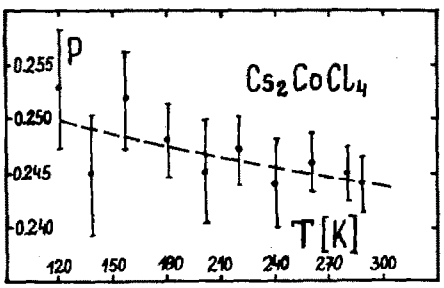

Fig. 4. Modulation parameter for Cs_2CoCl_4 vs. temperature

Partly supported through Project MR I.9.

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