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CONDUCTOMETRIC AND DSC EVIDENCE FOR A HIGH TEMPERATURE PHASE TRANSITION IN COBALT DIBROMIDE

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A solid-state phase transition in cobalt dibromide at 647 K has been revealed by three different alternative current techniques. A small thermal effect of (181±18) J mol^{-1} corresponding to the enthalpy of the transition has been determined by differential scanning calorimetry. The effect was observed on cooling and on heating as well.

Keywords: *cobalt dibromide, DSC, electrical conductivity, enthalpy of a high-temperature transition, phase transition*

Introduction

Most experimental and theoretical works on cobalt(II) halides deal with investigations of their room- or low-temperature properties in view of magnetic and optical properties of these compounds [1–6]. Little work has been concerned with high-temperature properties [7–11].

Anhydrous cobalt(II) bromide has a layered structure of the CdI_2 type [12], with a hexagonal close-packed array of Br^- ions and with Co^{2+} ions occupying half the octahedral holes [13]. These crystals show an antiferrromagnetic transition at 19 K [1].

In the measurements of heat capacity of cobalt(II) bromide, carried out in the range of temperature from 347 to 723 K, Wydeven and Gregory [14] observed an anomaly at about 643 K which they ascribed, on the basis of X-ray powder diffraction experiments, to a phase transition associated with a change from the hexagonal close-packed CdI_2 type structure to the cubic close-packed $CdCl_2$ type structure. The anomaly began at about 639 K and extended to about 657 K. The effect was reversible. The heat of transition was estimated to be (167±63) J mol^{-1}. No effect was observed on DTA cooling curves taken between 773 K and room temperature.

In this work we report that results of electrical conductivity measurements give reliable evidence for the high temperature phase transition described in [14]. Small but clear thermal effects on DSC curves, both on heating and on cooling, also confirm the transition in $CoBr_2$ at 647 K.

Experimental

Anhydrous $CoBr_2$ was obtained from the hexahydrate (98%, Aldrich). Water was being removed at first by heating gently the hydrate to 380 K in a vacuum dryer and next by heating under vacuum in an electric furnace to about 1000 K. The salt was stored in sealed ampoules.

Measurements of electrical conductivity were carried out under argon atmosphere, in capillary silica cells with cylindrical platinum electrodes and a Pt/Pt,Rh thermocouple fixed close to one of the electrode compartments [15, 16]. The cells were calibrated beforehand with a standard aqueous solution of potassium chloride (71.1352 g KCl/1000 g of the solution) [17]. The measurements began after melting of cobalt(II) bromide, filling up the capillary and thus getting an electrical contact between platinum electrodes. Several cycles of heating and cooling were performed, with a rate which did not exceed 1 K min^{-1}.

Electrical conductivity was measured using two kinds of conductivity meters:

- an *ac* bridge at 5 kHz [15, 18]. The dependence of the resistance on frequency in the range from 1 to 30 kHz was checked during each run and was found to be negligible. The temperature was measured twice using a Ni/Ni,Cr thermocouple, directly before and after equilibration of the bridge for resistance measurement.
- a conductivity meter CDM 230 Radiometer Analytical [19]. The frequency of applied alternating current was set automatically in a stepped manner between 94 and 46900 Hz, depending on a value of

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the resistance measured. A Pt/Pt,Rh thermocouple was used for temperature measurements. Conductivity and temperature were simultaneously registered by a computer every 10 s

Additionally, resistances *vs.* temperature were determined on the basis of impedance spectra. Measurements were performed under argon atmosphere, in silica cells with two platinum electrodes and a Pt/Pt,Rh thermocouple. Impedances were measured by Autolab Eco Chemie B.V. in the frequency range between 10 Hz and 1 MHz.

Differential scanning calorimetry experiments were carried out using a Mettler Toledo DSC 25 calorimeter [19, 20] cooperating with updated STAR^e software version 6.0. Anhydrous $CoBr_2$ was inserted, in a glove box, directly into small silica ampoules with flattened bottom, then used for DSC measurements after they had been sealed under vacuum. The heating or cooling rates used were from 0.5 to 20 K min^{-1}.

Results and discussion

Measurements of the electrical conductivity performed by the three methods: the classical alternative current bridge technique, the conductometer coupled with a computer and the impedance spectroscopy have given practically the same results. Dependence of the electrical conductivity of $CoBr_2$ on temperature confirms a high temperature solid-state transition in $CoBr_2$. Examples of conductivity curves are presented in Fig. 1. as a natural logarithm of specific conductivity of $CoBr_2$ *vs.* reciprocal of absolute temperature. The three plots are very similar.

The first very strong drop of the conductivity is observed on freezing, at the temperature of 950 K, and the second at 647 K, i.e. close to the temperature of a thermal effect reported by Wydeven and Gregory [14]. Next, as determined by impedance measurements, the conductivity regains the previous value and then falls down slowly.

It is striking that the conductivity of the high-temperature modification is relatively high, of the order of $10^{-1}\ \Omega^{-1}\ m^{-1}$, and does not change much in the range of about 200 K i.e. between around 850 and 650 K. However, when approaching the phase transition, in the range of the temperature between about 770 and 650 K, a clear tendency to a slight increase in the conductivity with decreasing temperature can be noticed on each of the three plots. The reason of this anomaly is not known yet.

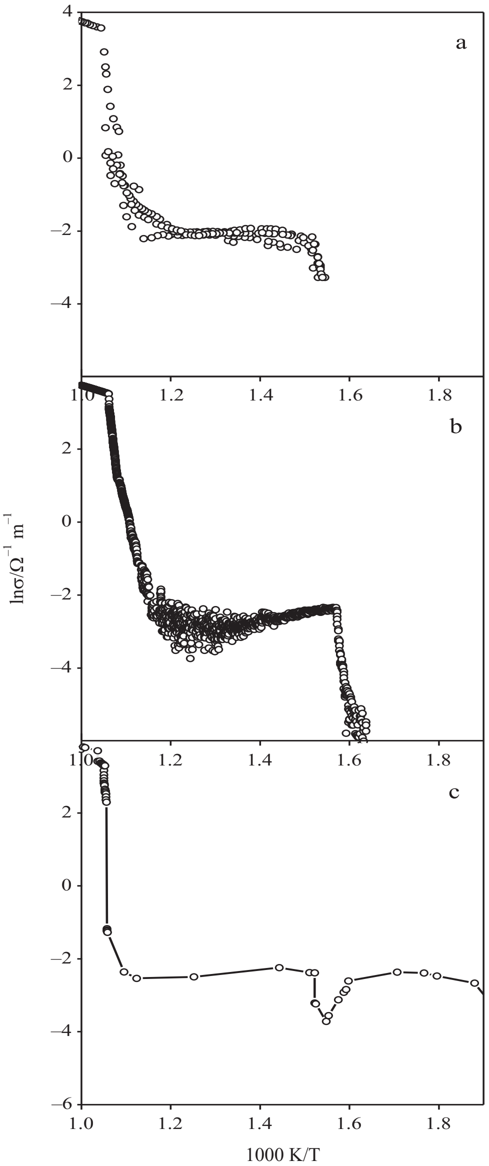

Fig. 1 Conductivity logarithm *vs.* reciprocal of temperatures as measured by a – an *ac* bridge, b – a conductometer, c – an impedance analyzer

A high temperature solid-state transition in cobalt(II) bromide can be identified as well by differential scanning calorimetry, provided that the sample has a considerable mass and heating or cooling rates are sufficiently fast (above 15 K min^{-1}). Examples of DSC scans with a heating and cooling rate of 15 K min^{-1} in the temperature range between 550 and 1000 K are presented in Fig. 2 for a sample of 104.1 mg $CoBr_2$. The thermal effect corresponding to a solid-state transition at 647 K as well as that of melting/freezing of anhydrous cobalt(II) bromide are observed. An estimated enthalpy of the transition (181±18) J mol^{-1} is close, within experimental error, to that given in [14]. Thus both the value of temperature and that of enthalpy of the thermal event, determined by differential scanning calorimetry confirm a high temperature phase transition in cobalt(II) bromide.

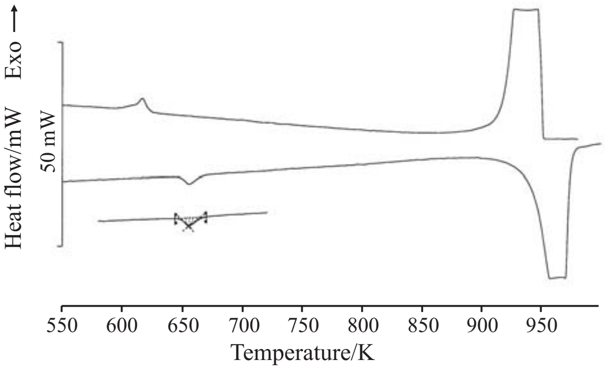

Fig. 2 DSC curves for 500–1000 K temperature range and heating or cooling rate of 15 K min^{-1}; inset: evaluation of the thermal effect corresponding to the solid-state transition

Conclusions

Because of the small thermal effect of the phase transition, the high-temperature modification of cobalt dibromide is difficult to detect by thermal methods. However, a relatively large mass of a DSC sample and a high heating or cooling rate allow the event to be observed.

On the other hand, electrical measurements reveal a distinct change of conductivity values around the phase transition temperature, providing more proof of the existence of two forms of cobalt dibromide. It should be noted, that future studies of electrical properties of the high-temperature form of cobalt dibromide would be of value, in view of unusual conductivity dependence on temperature for this phase.

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