Journal of Thermal Analysis and Calorimetry, Vol. 88 (2007) 2, 525–530

MELTING AND HIGH-TEMPERATURE SOLID STATE TRANSITIONS IN COBALT(II) HALIDES

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Melting and high temperature solid-state transitions in $CoCl_2$ and $CoBr_2$ are widely discussed. On the basis of DSC and conductometric measurements it was found that melting process of $CoCl_2$ is preceded by a solid-state transition appearing about 20 K below the melting point of $CoCl_2$. Due to deconvolution of the thermograms, the enthalpy of fusion and that of solid-state transition were found to be 36.4 and 9.6 kJ mol^{-1}, respectively. Melting points of $CoCl_2$ and $CoBr_2$ were established to be 999.0 and 949.7 K, respectively. Hitherto unknown enthalpy of fusion of $CoBr_2$ was determined to be 27.2 kJ mol^{-1}. A solid-state transition in $CoBr_2$ at 650 K has been confirmed.

Keywords: *cobalt dibromide, cobalt dichloride, DSC, electrical conductivity, enthalpy of fusion, solid-state transition*

Introduction

It is well known that cobalt(II) chloride and cobalt(II) bromide undergo antiferromagnetic phase transition at the Neel temperature of 24.5 and 18.9 K, respectively [1]. On account of their unusual magnetic properties, these salts have been studied for many decades mainly at low temperatures [1–12].

Since the late seventies of the XX century when ferroelectric modifications among alkali metal halozincates [13] and halocobaltates(II) [14] were discovered, a number of such ternary compounds have been also examined at higher temperatures [15–18]. Some of them, e.g. K_2CoCl_4 [15] or K_2CoBr_4 [16] show ferroelectricity above the room temperature. This may open for cobalt dihalides a large way of applications as initial substances for this kind of materials. It seems, however, that solid-state behaviour of the pure cobalt dihalides in this range of temperature, including melting transition, has not been thoroughly investigated.

The values of melting point of $CoCl_2$ given in the literature show a relatively wide spread, essentially between 989 and 1013 K, e. g. 989 K [19], 993.7±1.3 K [20], 994 K [21], 997 K [22], 1000 K [23], 1008±7 K [24], 1009±5 K [25], 1013 K [26–30]. According to Seifert [19], higher values of the melting point of $CoCl_2$ are obtained due to impurities by nickel dichloride while the lower ones arise from impurities by cobaltous oxide, appearing as a product of hydrolysis of $CoCl_2$ affected by water. It should be noted that the lowest values of 989 K [19] and 993.7 K [20] listed above were obtained from cooling curves and may be influenced by the effect of supercooling. Nevertheless, the highest value of 1013 K seems to be questionable. Recently [31], for thermodynamic evaluation and optimization of a multicomponent system of dichlorides, Robelin *et al.* [31] fixed the melting temperature of $CoCl_2$ to 997 K, the lowest experimental value given in JANAF Thermochemical Tables (3$^{\mathrm{rd.}}$ ed., 1985).

The early reported enthalpy of fusion of $CoCl_2$, based on the Kelley and Rossini Tables, was 30.9 kJ mol^{-1} [32]. The same value has been given in [23], a higher one 38 kJ mol^{-1} in [28] and still higher, but close each to other, values of 43.9, 44.8 and 45 kJ mol^{-1} in the data bases of Pankratz [21], Kubaschewski *et al.* [27] and recent CRC Handbook of Chemistry and Physics [33], respectively. The highest, strayed value of 59.0 kJ mol^{-1} was given by Barin and Knacke [26]. For thermodynamic evaluation and optimization of dichloride systems, Robelin *et al.* [31] used for $CoCl_2$ an estimated value of enthalpy of fusion of 43.920 kJ mol^{-1}.

The above discrepancies of the data on values of the melting point and of the heath of fusion for cobalt dichloride may arise from the fact that $CoCl_2$ probably exhibits a solid-state transition before melting. Existence of a second crystalline form of $CoCl_2$ had been already suggested by Basset and Badwell [24]. Next, the transition temperature was located at 953 K [28, 34] i.e. about 50 K below the melting point of the cobalt dibromide. Seifert [19] observed on DTA curves a weak thermal effect at this temperature but he was not able to confirm the existence of the second modification of $CoCl_2$ by the X-ray diffraction method. Nevertheless, respective

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1388–6150/$20.00

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invariances have been plotted on phase diagrams of the binary systems of cobalt dichloride with alkali metal chloride [19]. In case of the $CoCl_2$-LiCl system, the liquidus curve even showed a clear kink near the supposed transition temperature. Similar effect can also be observed in the $CoCl_2$-NaCl phase diagram given by Bolshakov *et al.* [35]. However, in a later paper [36], Seifert reported that the transition point of $CoCl_2$ could not be confirmed.

Differently to $CoCl_2$, there is a general agreement on the value of the melting point of $CoBr_2$. For the most part, the reported value is 951 K [30, 37, 38]. As far as the enthalpy of fusion for $CoBr_2$ is concerned, it seems that no experimental value is present in the literature. No information on this subject is included in such databases as for example 'Thermodynamic Properties of Halides' [21], 'Materials Thermochemistry' [27], 'CRC Handbook of Chemistry and Physics' [23, 33] or 'NIST Chemistry WebBook' [29].

A high-temperature solid-state transition in $CoBr_2$ was found in 1964 by Wydeven and Gregory [39]. An anomaly of the heat capacity of cobalt(II) bromide was observed from about 639 to 657 K and the heat of transition was estimated to be 167±63 J mol^{-1}. It should be noted that no thermal event appeared on DTA cooling curves [39] while X-ray powder diffractograms taken at 553±20 K showed the CdI_2-type structure ($P\bar{3}$ m1) and those taken at 716±20 K showed the $CdCl_2$-type structure ($R\bar{3}$ m). This transition has been quoted in few data sources [27, 40–42] but it seems that no experimental work has been done on it since the report of Wydeven and Gregory [39]. To our knowledge, the transition has not been considered in construction of respective phase diagrams with $CoBr_2$ as one of the components (e.g. in [38]).

The aim of our work was to study melting and high-temperature phase transitions of cobalt(II) chloride and cobalt(II) bromide, in order to determine the values of respective temperatures and heats of transitions. Differential scanning calorimetry and measurements of the electrical conductivity were applied. These methods are commonly used for phase transition studies [43–45]. Establishing this kind of data will allow us to evaluate thermodynamic properties of molten salt mixtures, based on measured liquidus temperatures [46].

Experimental

Preparation of anhydrous salts

Anhydrous cobalt(II) chloride and anhydrous cobalt(II) bromide were obtained from the respective hexahydrates: $CoCl_2 \cdot 6H_2O$ (98%, Aldrich) and $CoBr_2 \cdot 6H_2O$ (99%, Aldrich). Initially the hydrates were gently heated from room temperature to about 400 K in a vacuum dryer. Dehydration was completed by heating the salt slowly to melting under vacuum in an electric furnace. Anhydrous cobalt dihalides were cooled under argon and stored in sealed glass ampoules. Part of this material, used later for a few DSC samples, was sublimed and resublimed under vacuum in silica tubes.

Differential scanning calorimetry

Calorimetric measurements were performed with a Mettler Toledo DSC 25 measuring cell with TC15 TA Controller. Basic software STAR^e Version 6.0 complemented by a few optional Mettler Toledo programs were used to carry out the measurements and to read the results. The calorimeter was calibrated with melting points of indium, tin, lead, zinc and aluminum and with heat of melting of indium and zinc.

Samples for DSC measurements were prepared in a glove box Labmaster 130 MBraun, filled with dry argon (<1 ppm O_2, <4 ppm H_2O). Appropriate quantities of cobalt(II) chloride or cobalt(II) bromide were inserted into small silica ampoules, next sealed under vacuum. The ampoules had 6 mm in outer diameter and 14 mm in height, and had a flat, polished bottom. The mass of the introduced salt was between about 10 and 100 mg. An identical empty ampoule sealed under vacuum served as a reference. Prior to measurements, the samples were heated to melting and cooled slowly to the room temperature.

DSC runs were recorded with a particular heating rate between 0.1 and 15 K min^{-1} from the room temperature to above the melting point of the respective salt. For most cases, cooling curves were also taken in a similar range of temperature and with the cooling rate between 0.1 and 15 K min^{-1}.

Conductometric measurements

Measurements of electrical conductivity were performed in silica cells with a capillary between two cylindrical platinum electrodes [47]. The cells were adapted to measuring conductivity in both the liquid and the solid state and during crystallization or melting as well. Measurements were carried out under argon atmosphere in several heating and cooling cycles in an appropriate range of the temperature. Heating and cooling rates used did not exceed 1 K min^{-1}. The temperature was measured using a Pt/Pt,Rh thermocouple fixed close to one of the electrode compartments. The cells were calibrated beforehand with a standard aqueous solution of potassium chloride (71.1352 g KCl/1 kg of the solution [48, 49]). Electrical conductivity was measured using a conductometer CDM 230 Radiometer

Analytical [50]. The applied frequency of alternating current was set automatically, depending on the value of the resistance measured. Conductivity and temperature were simultaneously registered by a computer every 10 s. The results of the experiments were processed by a computer program, and presented as a natural logarithm of specific conductivity *vs.* reciprocal of absolute temperature.

Results and discussion

Examples of DSC curves for $CoCl_2$ in the vicinity of the melting/freezing transition, obtained on heating and on cooling are given in Fig. 1. DSC runs show the presence of overlapping peaks, corresponding probably to two thermal events, close to each other. A superposition of thermal effects was observed independently of whether a sample had been melted beforehand or used for measurements directly after resublimation. Two-steps process of solidification is also observed on the Arrhenius plot of temperature dependence of the conductivity for liquid and solid $CoCl_2$ (Fig. 2).

The peaks on DSC curves overlap the more, the higher the heating rate is (1 K min^{-1} in Fig. 1a; 10 K min^{-1} in Fig. 1b). However, the value of the melting point of $CoCl_2$, determined from these scans using the Purity option software (based on van't Hoff equation) is identical, viz. 999.0±2.2 K (1 K min^{-1}) and 999.0±1.5 K (10 K min^{-1}). On the other hand, upon cooling with a rate of 5 K min^{-1}, the peaks appear to be almost entirely separated (Fig. 1c) but, due to surfusion, reliable transition temperatures cannot be determined.

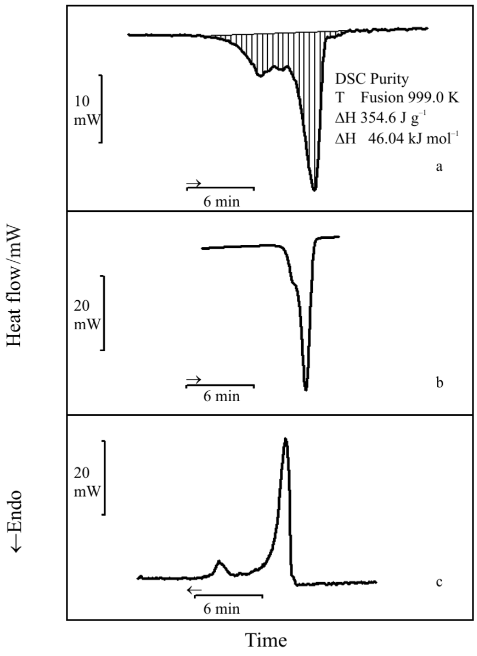

Fig. 1 a – Original DSC curves for $CoCl_2$, obtained on heating at 1 K min^{-1} and b – on heating at 10 K min^{-1}; c – example of an original DSC curve for $CoCl_2$, obtained on cooling at 5 K min^{-1}

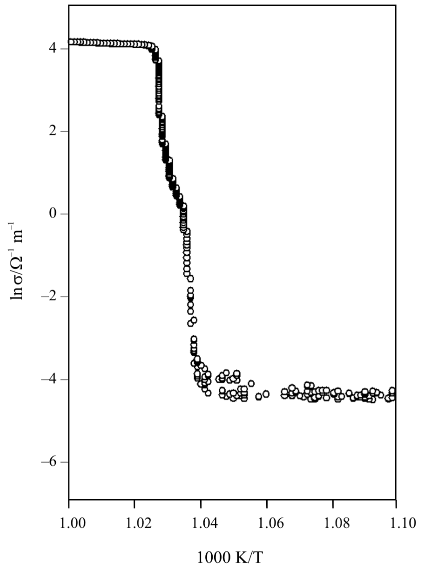

Fig. 2 Arrhenius plot of temperature (*T*) dependence of the conductivity (σ) for liquid and solid $CoCl_2$

Changes of the total enthalpy, as obtained by integration of the peaks area presented in Figs 1a, 1b and 1c, are 46.0, 29.2 and 31.5 kJ mol^{-1}, respectively. The highest value of 46.0 kJ mol^{-1} has been obtained for the lowest heating rate of 1 K min^{-1} of the DSC scan (Fig. 1a). This value is very close to these for the enthalpy of melting of $CoCl_2$, recommended by known sources of the thermochemical data, e.g. [21, 27, 31, 33]. It seems, however, that considering the peak shape, this value is the sum of the enthalpy of melting and of the enthalpy of a solid-state transition taking place in the proximity of melting.

In order to determine the overlapping peak positions and areas, a curve fitting analysis for DSC curves of $CoCl_2$ was carried out. The fit of the DSC curve for $CoCl_2$ presented in Fig. 1a to an EMG (Exponentially Modified Gaussian) type curve, in the range of temperature between 900 and 1020 K, is given in Fig. 3a and a deconvolved signal, calculated using EMG (Exponentially Modified Gaussian), is given in Fig. 3b. The onset temperature of the first endotherm 979±2 K was taken as the temperature of a solid-state transition. The values of the enthalpy of this transition and that of fusion were found to be 9.6±1.0 and 36.4±1.0 kJ mol^{-1}, respectively.

Example of a DSC melting curve for $CoBr_2$, obtained at a heating rate of 2 K min^{-1}, is given in Fig. 4a. Melting point of $CoBr_2$, determined using the Purity software, is 949.7±0.2 K, in accordance with literature data [30, 37, 38]. Integration of the peak area gives a value of 27.2±1.0 kJ mol^{-1} for the enthalpy of fusion of $CoBr_2$. A baseline shift correction of the heat flow curve for $CoBr_2$ had been made before fitting the DSC scan to an EMG (Exponentially Modified Gaussian) type curve (Fig. 4b).

Dependence of the electrical conductivity of $CoBr_2$ on temperature shows two strong reversible changes: at the melting point and at about 300 K below the melting point (Fig. 5). Similar results were obtained by using an alternative current RC bridge or the impedance spectroscopy [51]. An impressive change in the conductivity appearing at about 640 K, i.e. inside the range of temperature given by Wydeven and Gregory [39] for an anomaly of the heat capacity run, confirms the existence of a high-temperature phase transition in $CoBr_2$.

DSC scans, performed with a sufficiently high rate of heating or cooling (Fig. 6), also reveal this solid-state transition, contrary to DTA curves applied in [39]. Enthalpy change associated with this transition is 0.18±0.02 kJ mol^{-1}.

DSC curves for $CoCl_2$, traced in the vicinity of melting, both *vs.* time (Fig. 1) and *vs.* temperature (Fig. 2),

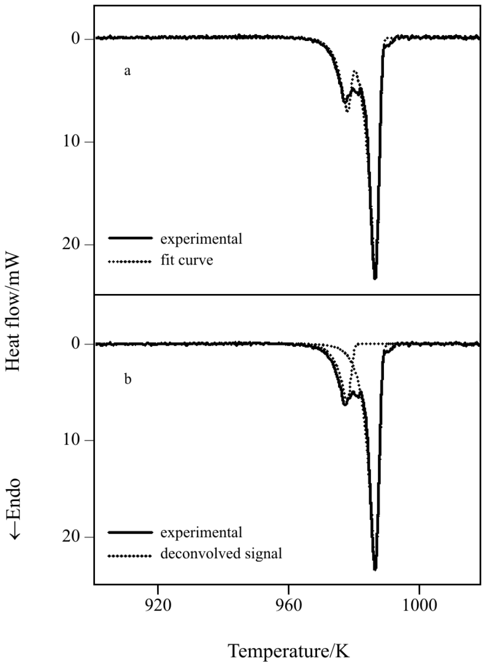

Fig. 3 Fit of the DSC curve for $CoCl_2$ presented in Fig. 1a to an a – EMG (Exponentially Modified Gaussian) type curve; b – deconvolution of the signal presented in Fig. 1a

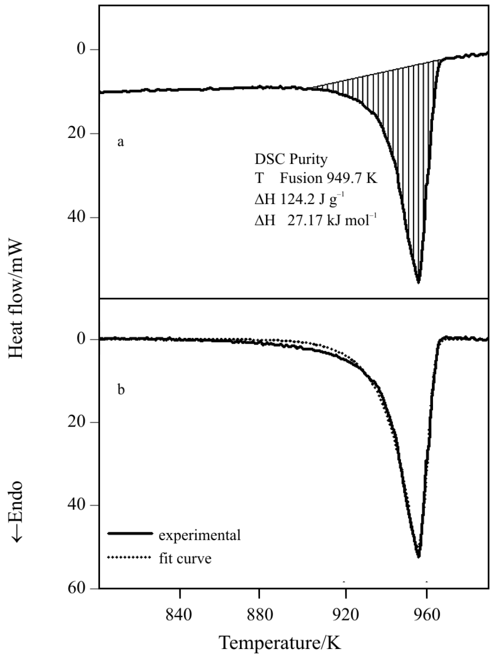

Fig. 4 a – DSC melting curve for $CoBr_2$, obtained at 2 K min^{-1}; b – fit of the DSC melting curve for $CoBr_2$, with baseline correction, to an EMG (Exponentially Modified Gaussian) type curve

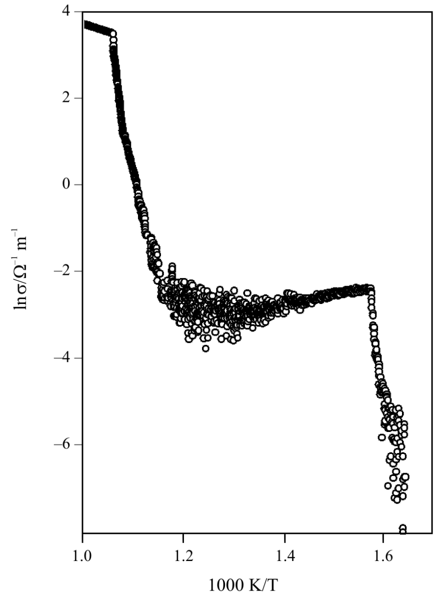

Fig. 5 Arrhenius plot of temperature (*T*) dependence of the conductivity (σ) for liquid and solid $CoBr_2$

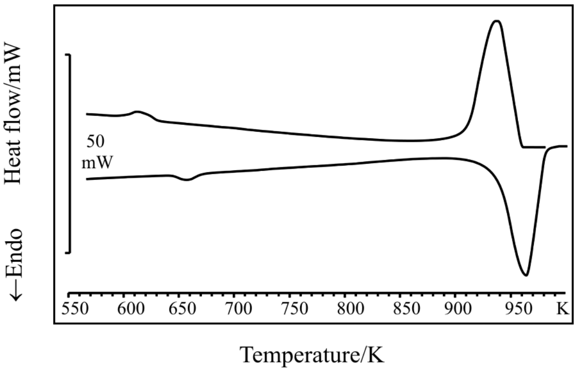

Fig. 6 DSC curves for $CoBr_2$, obtained in the temperature range between 550 and 1000 K at heating/cooling rate of 15 K min^{-1}, and showing as well fusion/crystallisation as solid-state transitions

show that two thermal events take place in this area. Consideration for only one event could be the reason of a large spread of values of the melting point as well as these of the enthalpy of fusion given in the literature for this salt.

Our results indicate the melting point of $CoCl_2$ to be 999±2 K and a total change of the enthalpy during transition to be 46.0±2.0 kJ mol^{-1}, close to values accepted e.g. in [31]. Deconvolution (Fig. 3b) of the signal presented in Fig. 1a gives 9.6±2.0 kJ mol^{-1} and 36.4±2.0 kJ mol^{-1} for the enthalpy of a solid-state transition and the enthalpy of fusion, respectively.

The nature of this solid-state transition is not known. At room temperature, $CoCl_2$ has the $CdCl_2$-type structure ($R\bar{3}m$), in which cobalt(II) ions are octahedrally coordinated. A change in the coordination symmetry around the Co(II) ion from octahedral to tetrahedral, when passing to the molten state, was observed on the basis of measurements of the magnetic susceptibility [52] and absorption spectra [53]. Thus, we can suppose that the solid-state transition which starts about 20 kelvins below the melting point may be connected with such a structural change. It should be noted, however, that according to Trutia and Musa [53] a new absorption band indicating the presence of a tetrahedral complex $[CoCl_4]^{2-}$ appears already at 920 K i.e. about 80 kelvins below the melting point. Our DSC thermograms do not show any phase transition of $CoCl_2$ between room temperature and 979 K.

A solid-state phase transition undergoing just prior to melting, like that in $CoCl_2$, has been found in $SrBr_2$ by means of drop calorimetry [54] and confirmed later by DTA [55] and DSC [56] methods. This may be a reason for which $SrBr_2$ exhibits unusually low entropy of fusion 11.3 J K^{-1} mol^{-1} [54]. In case of $CoCl_2$, which has a different, layer type structure, the value of 36.4 J K^{-1} mol^{-1} for entropy of fusion was found to be similar to these for cadmium dihalides [27]: 36.2 and 39.8 J K^{-1} mol^{-1} for $CdCl_2$ and $CdBr_2$, respectively. In the light of these facts, a value of entropy of fusion 46.0 J K^{-1} mol^{-1}, based on the total enthalpy change of 46.0 kJ mol^{-1}, seems not likely.

Melting point of $CoBr_2$ and its enthalpy of fusion was established to be 949.7±0.2 K and 27.2±0.2 kJ mol^{-1}, respectively. A considerable shift of the baseline (Fig. 4a), resulting in an important increase of the heat capacity of molten $CoBr_2$ in comparison with the solid, has been observed. To our knowledge, neither the enthalpy of fusion nor the heat capacity of liquid $CoBr_2$ have been reported till now.

It has been confirmed in this work that $CoBr_2$ exhibits a solid-state transition near 640 K [39]. Reversible changes around this temperature have been shown on DSC (Fig. 6) and conductivity curves (Fig. 5). The thermal effect of 0.18 kJ mol^{-1} associated with this transition is about 150 times lower than the enthalpy of melting of $CoBr_2$. Together with insignificant entropy of transition 0.28 J K^{-1} mol^{-1}, this might suggest the possibility of a second-order transition [57]. However, X-ray diffraction analysis [39] indicates that the process involves a change in crystal structure like a first-order transition.

In contrast to a small thermal effect, a drop of the electrical conductivity upon transition from a high-temperature $CdCl_2$-type phase to the low-temperature CdI_2-type phase of $CoBr_2$ is very strong. It is common that phases with layer type structures can exhibit big differences in electrical properties while recognition of differences in their crystallographical features may often be difficult. A relatively high electrical conductivity of the high-temperature form of $CoBr_2$ may indicate rather large entropy of the solid, possibly due to a considerable disorder, and consequently, the low entropy of melting. This latter was found to be 28.6 J K^{-1} mol^{-1}, a value situated below these for $CdCl_2$ or $CdBr_2$ [27].

Conclusions

Values of enthalpy of fusion of $CoCl_2$ given in the literature for the most part are much higher (around 44 kJ mol^{-1}) than that of 36.4 kJ mol^{-1}, determined in this work. Apparently, due to the superposition of the two events, both the enthalpy of the solid-state transition, appearing about 20 kelvins below the melting point 999 K, and the enthalpy of fusion have been included in those values. The enthalpy of a thermal event preceding melting was found to be 9.6 kJ mol^{-1}.

The value of the entropy of fusion for $CoCl_2$ 36.4 J K^{-1} mol^{-1}, based on the enthalpy change of 36.4 kJ mol^{-1} given above, resembles closely that for isostructural cadmium dichloride. In contrast, a value of the entropy of fusion for $CoBr_2$ 28.6 J K^{-1} mol^{-1}, based on the enthalpy of fusion 27.2 kJ mol^{-1}, reported for the first time in this work, is lower than that for cadmium dichloride, suggested to be isostructural with a high temperature form of $CoBr_2$ [39]. This last appears about 300 kelvins below the melting point 949.7 K and probably exhibits an enhanced disorder, resulting in a relatively high electrical conductivity and a lower change of entropy on melting.

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DOI: 10.1007/s10973-006-8000-9