Intercalation Compounds of Large Organic Molecular Cations in the Layered Dichalcogenide 2H-TaS$_2$

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Dedicated to Prof. Dr. Wolfgang Jeitschko on the occasion of his 60th birthday

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We report on the first successful intercalation of organic cations in large crystals of 2H-TaS$_2$ by electrochemical methods. The following species have been intercalated: Tetramethylammonium, methylviologen and methylene blue. Whereas the first species can be intercalated in chemical equilibrium like the hydrated metal ions, the intercalation of the other two more complex cations is accompanied by side reactions. The most complex system is methylene blue/TaS$_2$ where we observe three different phases depending on the preparation conditions. The electrical resistivity as a function of temperature has been measured by a 4-point ac method on single crystals immediately after intercalation. All samples are superconductors, some of them having a transition temperature to the superconducting state $T_c$ of 4.9 K, which is quite high for organic molecule intercalation compounds of 2H-TaS$_2$. The anomaly of the resistivity at 77 K in the empty host lattice is suppressed in all of the intercalated samples even at the very low charge transfer of $n = 0.06$.

Introduction

Shortly after the beginning of intercalation chemistry of the layered metal dichalcogenides a large number of organic molecules have been intercalated in 2H-TaS$_2$ and the products have been tested for superconductivity [1]. Only a few of these compounds have been studied afterwards in detail [2–4], probably due to the lack of homogeneously intercalated crystals of high quality.

From our investigation of hydrated metal intercalation compounds [5] we know that it is possible to obtain intercalated crystals of high quality by electrointerecalation from aqueous solutions at room temperature (residual resistivity ratio RRR = $R_{300K}/R_{4.2K}$ of 20 - 40 for $K_x(\text{H}_2\text{O})_y\text{TaS}_2$ [6]; for comparison the empty host lattice shows a RRR of 70 - 90 [6], and RRR of 2 for the pyridine intercalation compound [2]). This very soft electrochemical method of preparation could help to overcome the restriction of the intercalated organic molecules to amines and N-containing heterocycles and to small molecules. On the other hand, this method requires the existence of stable catonic species which can be dissolved in polar liquids to form electrolyte solutions. The first electrochemical intercalation of organic species (pyridinium and anilinium ions) was described by Subba Rao and Tsang [7]. Schöllhorn et al. [8] extended this method to a series of organic cations like the tropilium cation, rhodamine B, and a triphenylcarbonium dye. Both studies are restricted to the intercalation of powders and the samples are not characterised further with exception of the layer distance.

Beside the protonated amines and heterocycles many species are forming stable cations whose salts can be dissolved easily in water; such species are the quaternary ammonium ions, or some families of dyes like the triphenylcarbonium systems, the phenothiazines etc. Some of these molecular cations are quite large and have an extended $\pi$-electron system. Such extended cations should favour a low charge transfer due to the packing possibilities of the cations. Therefore, we could check the existence of a charge density wave (CDW) as proposed by DiSalvo for some organic intercalation compounds [9]. In addition these systems may show new exciting phenomena:

- There could be an overlap between the $\pi$-orbitals of the dye molecules and the conduction band of

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the metal layers making the compound physically more three-dimensional;
- An enhancement of the in-plane conductivity by light absorption of the dye molecules may occur;
- If the \( \pi \)-orbitals of the dye neighbours overlap with each other it may be possible that they form their own band;
- These dye intercalation compounds could be model systems for exciton superconductivity [10].

Until now only a few molecules with extended \( \pi \)-electron systems were intercalated in 2H-\( \text{TaS}_2 \); Schöllhorn et al. [8] reported on the electrointercalation of rhodamine B and fuchsin into a powder sample; Preobrazhensky et al. [11] described the thermal intercalation of copper phthalocyanine in 2H-\( \text{TaS}_2 \)-powder; from this compound the layer distance, the intercalate content and \( T_c \) are known. We report in this paper on the first successful electrointercalation of organic cations into crystals large enough for the measurement of the electrical resistivity. Beside the very stable tetramethylammonium cation TMA\(^+\) we intercalated the much larger molecular cations with the extended \( \pi \)-electron systems methylviologen (MV\(^{2+}\)) and methylene blue (MB\(^+\)). The samples were characterised by the in-situ measurement of the crystal expansion during the intercalation reaction, the layer distances and the chemical analysis. In addition, we determined the electrical resistivity of samples by a four-point ac-method as a function of temperature.

**Experimental**

**Preparation**

2H-\( \text{TaS}_2 \) was prepared by iodine vapour transport and a subsequent annealing procedure. For intercalation we only used crystals of 1 - 2 mm in diameter, a thickness of around 50 \( \mu \)m, and a weight of 0.5 - 1 mg.

All intercalation reactions were carried out by electrochemical methods under galvanostatic conditions out of deaerated aqueous solutions under argon. TMA was intercalated at a current density of 5 mA/cm\(^2\) out of a solution of TMA bromide with a concentration of 0.1 M.

The dye intercalation compounds were prepared from 1 mM solutions. For a successful intercalation a current in the order of 10 - 20 \( \mu \)A had to be applied. To avoid too many cracks in the crystal due to the very high current density and in order to obtain a quantitative intercalation, the current was stopped every 990 s for the same period of time. The electrochemical potential was measured versus a saturated calomel electrode (SCE) and the intercalation was followed in situ by a dilatometer as described in [12].

**Characterisation**

As the electrochemical intercalation of the dye molecules was not in chemical equilibrium, there is no possibility to extract information about the charge transfer. Therefore, a chemical analysis of the dye content was necessary (carried out by Mikroanalytisches Labor Pascher, Remagen).

Crystallographic data were obtained from a Debye-Scherrer powder diagram using Ni filtered Cu Ka radiation.

The measurements of the in-plane resistivity were done with a 4-point-ac-method similar to the one used in [13]. The electrical contacts were made with thin gold wires connected to the samples with silver or gold paint. Care was taken to obtain a homogeneous current distribution. All resistivity measurements, if not particularly stated, were done directly after intercalation.

**Results and Interpretation**

Typical potential versus time (charge transfer) curves monitored during electrointercalation of TMA\(^+\) and of the methylviologen (a dication) are shown in Fig. 1. The potential curve of the TMA (Fig. 1, top) is very similar to that observed during the intercalation of hydrated metal ions [5]. It shows
a sequence of two two-phase regions (nearly constant potential) followed by a single phase region (decreasing potential with increase of charge transfer). For this curve the time scale is transformed by means of Faraday’s law into the charge transfer n. In contrast to the hydrated metal intercalation the onset of the single phase region is shifted from n = 0.27 to n = 0.21. Further details of the chemistry of this intercalation compound are described elsewhere [14].

The potential curve of the MV intercalation (Fig. 1, bottom) differs strongly from that of the TMA system. First, the above mentioned transformation of intercalation time into the charge transfer is not meaningful in this case; we would obtain a charge transfer much higher than 1e⁻/TaS₂ at the state when the crystal expansion is finished; this value is much too high for a reasonable packing density of the large cations. This unreasonably high charge transfer is a strong indication for severe side reactions accompanying the intercalation. Therefore, we had to apply an intercalation current twice as high as in the case of the TMA ion. Second, the electrochemical potential measured during current flow through the cell is strongly different from that observed after interruption of current flow. This is strong evidence for deviation from chemical equilibrium not observed in the intercalation of TMA. The simultaneous monitoring of the crystal expansion is essential for controlling the success of intercalation and to determine the end of the reaction (no further increase of crystal thickness).

The intercalation of methylene blue shows nearly the same features. But in contrast to methyliovigen one can get three different phases depending on the detailed reaction conditions. They are called the 9, 12 and 17 Å-phase in relation to the layer distances observed. The 17 Å phase could not yet be obtained as an homogeneous sample. The main difference in the preparation conditions of the other two phases is the intercalation current. For the 9 Å phase a current of 5 µA is sufficient while for the 12 Å phase the intercalation current is 20 µA and care must be taken to exclude light and oxygen. The reaction is successful only in a freshly prepared electrolyte solution.

The data characterising the compounds studied are collected in Table I.

The charge transfer n can be deduced from the electrointercalation experiment for the TMA intercalation compound only. In the case of the MV intercalation compound we can extract n from the electrochemical deintercalation; it amounts to n = 0.12. For the MB compounds both methods do not give reasonable charge transfer values.

The chemical analysis of the TMA intercalation compound yields an intercalate content of x = 0.21 in excellent agreement with the charge transfer n = 0.2 (the equivalence of both values is due to the fact that TMA is a monovalent cation like the alkali metal ions). The content of MV and MB is much lower; x = 0.06. In the case of MB we determined x only for the 9Å phase. Considering the charge transfer given above we conclude that MV is intercalated as the dication, also present in the intercalation solution. For the MB intercalation compound we calculate a charge transfer of 0.06 assuming that MB is intercalated as a monocation, as it is present in the solution. Preliminary determination of the C/N ratios leads to the conclusion, that the molecular cations in the interlayer space are not chemically altered. Taken this information together, we are led to the following compositions of the compounds studied:

(TMA⁺)₀.₂₁[TaS₂]⁻₀.₂¹
(MB⁺)₀.₀₆[TaS₂]⁻₀.₀₆
(MV²⁺)₀.₀₆[TaS₂]⁻₀.₁₂

The hydrogen content found in the intercalation compounds is always higher than expected from the content of the intercalated species, indicating that some additional water is cointercalated with the organic cations.

<table>
<thead>
<tr>
<th></th>
<th>X-ray data</th>
<th>Intercalate content</th>
<th>Charge transfer</th>
<th>Resistivity measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA⁺</td>
<td>3.35</td>
<td>2 × 1.15</td>
<td>0.21</td>
<td>0.2</td>
</tr>
<tr>
<td>MB⁺</td>
<td>9Å 3.33</td>
<td>2 × 1.91</td>
<td>0.06</td>
<td>0.06⁷</td>
</tr>
<tr>
<td>12Å 3.31</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17Å 3.31</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MV²⁺</td>
<td>3.34</td>
<td>2 × 1.91</td>
<td>0.06</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Tab. I. Unit cell dimensions, intercalate content and data taken from the resistivity measurements for the intercalation compounds of organic cations into 2H-TaS₂.

⁷ estimated from charge intercalation content.
As in the case of most other intercalation compounds of \(2\)H-TaS\(_2\) the a-axis of the host lattice is not strongly affected by the guest molecules. The crystal expansions measured by in situ dilatometry are in good agreement with the layer distances given in Table 1. All compounds are first stage phases. The layer distance of the TMA compound is in good agreement with the value given for powder samples in the literature \([15,16]\). It is slightly smaller than expected from the size of the TMA ion observed in an aqueous solution.

The small layer distance of the intercalation compounds of MV and MB (about 9 Å) can be explained only if the molecules are arranged with the aromatic ring systems parallel to the host layers. Even in this case the layer separation is quite small considering the van der Waals thickness of benzene and the thickness of the methyl groups in the periphery of the molecules. In the case of the 12 and 17 Å phases of the MB intercalation compound the molecules must be arranged with the ring systems perpendicular to the host layers or tilted in a complex way. A preliminary investigation of the 17 Å phase leads to the conclusion that the 17 Å phase is very unstable and easily transforms to the 12 Å phase.

The resistivity measured as a function of temperature for the compound \((\text{TMA}^+)_{0.21} \text{[TaS}_2\text{]}^{0.21}\) is shown in Fig. 2. The upper curve represents the resistivity of the sample measured immediately after preparation while for the lower curve the same sample was stored one day at room temperature under helium atmosphere. While the as prepared sample has a narrow transition to the superconducting state at 3.1 K, the transition of the aged sample is broader with a \(T_c\) of 3.4 K. But the residual resistivity ratio RRR rises from 15 to 26 for the aged sample. The resistivity anomaly observed at 77 K for the empty host lattice is not longer visible indicating the complete suppression of the CDW. There is a new anomaly in the resistivity just below room temperature, probably caused by freezing of the reorientational motion of the TMA ions.

The \(T_c\) value of 3.1 K for the TMA intercalation compound is different from those reported in literature: 2.9 K in \([15]\) and 3.7 K in \([16]\). This can be caused by the different preparation methods applied, different definitions of \(T_c\), or different handling of the samples before the measurement of \(T_c\). The transition width \(\Delta T_c\) of our sample amounts to 0.3 K, and is thus very sharp in comparison to most of the organic intercalation compounds studied. It is much broader \((\Delta T_c = 0.6 K)\) in the aged sample indicating some disorder or inhomogeneity inspite of the fact that RRR is higher.

The resistivity measured as a function of temperature for the 9 Å phase of \((\text{MB})_{0.06} \text{[TaS}_2\text{]}\) and for \((\text{MV})_{0.06} \text{[TaS}_2\text{]}\) (see Fig. 3) shows nearly the same features despite the different charge transfer and is very similar to the curve for the TMA intercalation compound. The residual resistivity ratio for the MB compound is 13, for the MV compound it amounts to 16, even higher than for the pyridine intercalation compound. The resistivity anomaly at 77 K observable in \(2\)H-TaS\(_2\) (and ascribed to a CDW) is absent as in all other intercalation compounds. Since the samples described in this paper show different charge transfer values down to 0.06 we can state that the CDW is suppressed even in much lower charge transfer regions than previously studied.
The $T_c$ values of 4.9 K for both compounds are much higher than that of the TMA compound. They are among the highest values known for molecular intercalation compounds with the exception of the DMA intercalation compound [3]. The reason for the very high $T_c$ values in these compounds is not quite clear. One reason could be the small charge transfer $n$. According to the band structure of 2H-TaS$_2$, assuming a rigid band model we would expect that after suppression of the CDW the density of states decreases with increasing charge transfer, thus leading to higher $T_c$ values for lower and a decrease of $T_c$ values with increasing $n$. In such a picture, however, it cannot be explained why both samples have the same $T_c$ despite the different charge transfer.

Conclusions

We have shown that it is possible to intercalate large organic species by a soft method in large crystals of 2H-TaS$_2$. The samples obtained show a reasonable homogeneity. None of the compounds exhibit a CDW phase transition, but they are superconductors, some of them with a very high $T_c$. We do not know whether these values are due to interactions of the extended $\pi$-electron systems with the conduction band of the host lattice. In order to study such a possibility additional measurements like the determination of the resistivity perpendicular to the layers, the anisotropy of the critical fields, or the optical properties of the intercalated molecules, are necessary and under way.