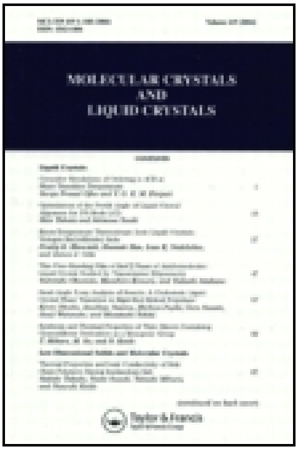

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W. Olberding [a], P. Ganal [b], G. Ouvrard [b] & T. Butz [c]

[a] Walther-Meifiner Institut für Tieftemperaturforschung der Bayerischen Akademie der Wissenschaften, 8046, Garching, FRG

[b] Institut des Matérianx de Nantes, 44072, Nantes, France

[c] Universität Leipzig, Fachbereich Physik, D-0-7010, Leipzig, FRG

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AMBIENT TEMPERATURE INTERCALATION OF Na AND In INTO TaS_2

W. OLBERDING, P. GANAL[+], G. OUVRARD[+], and T. BUTZ[++]

Walther-Meißner Institut für Tieftemperaturforschung
der Bayerischen Akademie der Wissenschaften, 8046 Garching, FRG
[+] Institut des Matériaux de Nantes, 44072 Nantes, France
[++] Universität Leipzig, Fachbereich Physik, D-0-7010 Leipzig, FRG

Abstract We report on ambient temperature intercalation of Na and In into TaS_2 (2H and 1T) using liquid metal eutectics and amalgams ($In_{0.17}Ga_{0.83}$, $In_{0.5}Hg_{0.5}$, $Sn_{0.15}Ga_{0.85}$, and Na_xHg). The intercalation process was monitored in situ by measuring the ^{181}Ta nuclear-quadrupole-interaction (NQI) via time differential perturbed angular correlation (TDPAC). At ambient temperature, a single metal species is intercalated selectively. The final products were found to be comparable to those obtained by high temperature synthesis. In the case of 1T-TaS_2, a soft chemistry induced Ta-coordination change from octahedral to trigonal-prismatic was observed.

INTRODUCTION

Intercalation of alkali metals and post transition metals into layered transition metal dichalcogenides has been studied intensively in the past[1,2]. In many cases the intercalation products were obtained by high temperature synthesis[2,3].

However, there are cases, e.g. the intercalation into 1T-TaS_2, where low temperature procedures can be applied only (1T-TaS_2 transforms irreversibly to 2H-TaS_2 at temperatures exceeding 463 K). In addition, intercalation at ambient or moderate temperatures often allows to study the formation of intermediate phases[1,4] and - starting with different host material polytypes - to derive different polytypes of the intercalation product[5].

Since TaS_2 reacts readily with liquid alkali or post transition metals, one strategy to perform ambient temperature intercalation might be the use of liquid eutectics. However, in this case the degree of cointercalation is not evident a priori, since in general both metal species may be intercalated from the eutectic. In order to settle this question we monitored in situ the intercalation process by measuring the ^{181}Ta ($I=5/2$) nuclear-quadrupole-interaction (NQI) via time differential perturbed angular correlation (TDPAC). The TDPAC-experiments were corroborated by X-ray powder diffraction and electron microprobe analysis.

EXPERIMENTAL

1T-TaS_2 and 2H-TaS_2 crystals were grown directly from the elements using iodine vapour transport[6]. In order to determine the ^{181}Ta (I=5/2) NQI by TDPAC we doped our materials with about 200 ppm neutron activated Hf-metal (containing ^{181}Hf with $T_{1/2}$ = 42d, the mother isotope of ^{181}Ta) during crystal growth. Small samples of uniform crystal size (ranging from 315μm up to 10mm) were sealed in quartz ampoules with usually a large excess of liquid eutectic and mixed carefully. Subsequently, the samples were placed between the γ-detectors of conventional 4-detector TDPAC setups equipped with either BaF_2 or NaI(Tl) scintillator crystals. In order to ensure a good contact with the liquid eutectic we stirred the samples from time to time. No specific care was taken concerning the relative orientation of the TaS_2-crystals. For further details about the TDPAC-technique, the data reduction and the data analysis we refer to A. Lerf and T. Butz[7] and the references given therein.

INDIUM INTERCALATION INTO 2H-TaS_2

from an $In_{0.17}Ga_{0.83}$ – Eutectic

2H-TaS_2 reacts with $In_{0.17}Ga_{0.83}$ already at room temperature: after mixing the crystals (Ø~1mm) with the liquid eutectic a new frequency component gradually appeared at ω_1 ~ 583 Mrad/s (Fig. 1, left), while the signal of the pristine 2H-TaS_2 (ω_0 ~818 Mrad/s) decreased. After 400 hours reaction time a homogeneous product with a c-parameter of 8.75Å was obtained. No peak migration was observable. This indicates a constant intercalate packing density throughout the entire reaction.

When we worked with only a small eutectic excess, the eutectic solidified after some time, indicating that a single metal species had intercalated. In fact, electron microprobe analysis on freshly cleaved crystals proved that mainly In was intercalated from the eutectic yielding $In_{1.0}TaS_2$. The amount of cointercalated Ga was found to be less than 6%. Both, the observed precession frequency ω_1 and the c-parameter (see Table 1) are identical to those of $In_{1.0}TaS_2$.[2,8,9] Moreover, after separating the crystals from the excess eutectic we observed the same variation of the ^{181}Ta-NQI signal versus temperature as for pure $In_{1.0}TaS_2$.[8,9] In particular, we also observed the same reversible phase transition near 510 K (Fig. 1, right). The transition temperature was, however, less defined if the crystals were kept in contact with the excess eutectic.

In some cases a small contribution of an intermediate phase could be detected during intercalation, whose precession frequency and c-parameter (ω = 480 Mrad/s, c = 8.0 Å) resembled that of $In_{2/3}TaS_2$.[9]

Unlike the $In_{0.17}Ga_{0.83}$ eutectic we could not observe any reaction between $2H\text{-}TaS_2$ and a similar $Sn_{0.15}Ga_{0.85}$ eutectic.

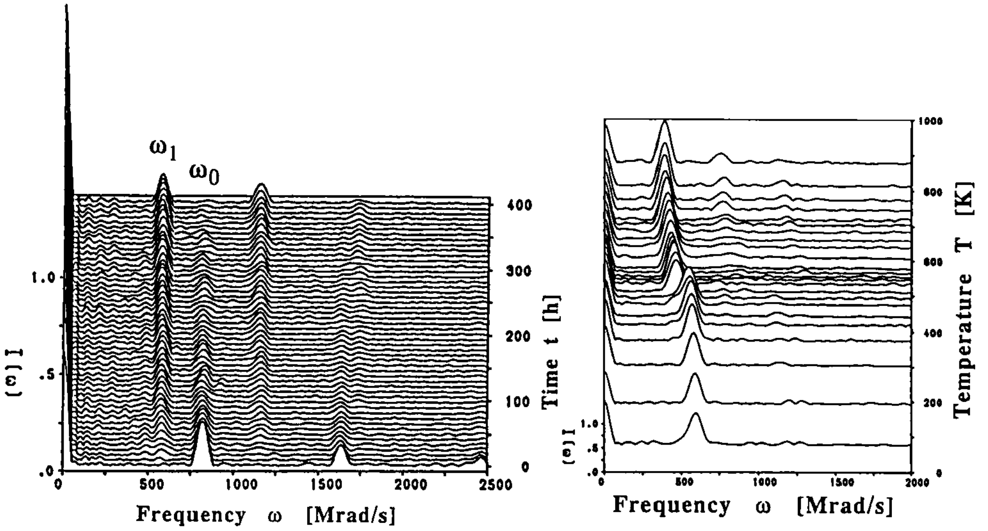

FIGURE 1 Left: in situ TDPAC study of the ambient temperature indium intercalation into $2H\text{-}TaS_2$ from an $In_{0.17}Ga_{0.83}$ eutectic. Right: stacked plot of Fourier transformed TDPAC-spectra versus temperature, showing a phase transition around 510 K.

from an $In_{0.5}Hg_{0.5}$ – Amalgam

$2H\text{-}TaS_2$ reacted in contact with a liquid $In_{0.5}Hg_{0.5}$ amalgam in a very similar way as with $In_{0.17}Ga_{0.83}$: upon intercalation the precession frequencies of an intermediate phase (~ 480 Mrad/s) and of the final product (580 Mrad/s, $c = 8.75$ Å) appeared, which we again attribute to $In_{2/3}TaS_2$ and $In_{1.0}TaS_2$, respectively. Electron microprobe analysis on freshly cleaved crystals confirmed that mainly In is intercalated. The amount of cointercalated Hg was found to be smaller than 5%. As for pure $In_{1.0}TaS_2$ the final product exhibited a reversible phase transition at about 510 K. However, the hysteresis of the phase transition was considerably larger than that found for $In_{1.0}TaS_2$ prepared either via high temperature synthesis[8,9] or via the $In_{0.17}Ga_{0.83}$ eutectic.

SODIUM INTERCALATION INTO $2H\text{-}TaS_2$ AND $1T\text{-}TaS_2$

Mercury forms a liquid amalgam at room temperature if mixed with less than 6% sodium (atomic percent). If brought into contact with the amalgam, both $1T\text{-}TaS_2$ and $2H\text{-}TaS_2$ react immediately. Although the final products after a reaction period of a month were quite similar with respect to their NQI-signals (Fig. 2, middle, Table 1) and their c-parameters (c=7.29 Å in both cases), the intercalation process itself was very different, as will be described in the following two subsections.

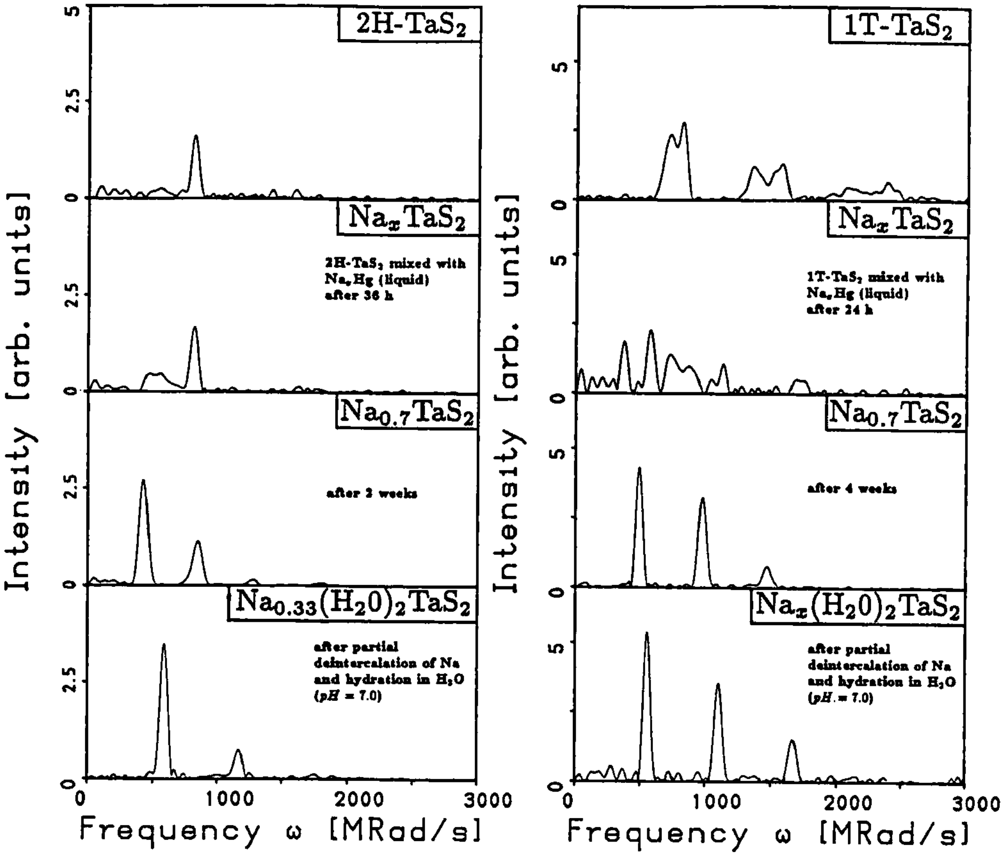

FIGURE 2 Fourier transformed TDPAC spectra for the empty host lattices (top), partially and fully Na intercalated TaS_2 (middle), and subsequently hydrated (pH=7) compounds (bottom) with 2H-TaS_2 (left) and 1T-TaS_2 (right) as starting materials. Intensity differences between the 1T-TaS_2 and 2H-TaS_2 intercalation experiment are purely experimental and mainly due to the different time resolution of the used TDPAC-setups.

Na – Intercalation into 2H-TaS_2

In the case of 2H-TaS_2 we observed a similar reaction as for the chemical lithiation via butyllithium[4]: during intercalation several discrete precession frequencies appeared consecutively (Fig. 2, left), which we attribute to the formation of intermediate phases and the final product, respectively. X-ray powder diffraction diagrams and the NQI-signal of the highly hygroscopic product were found to be identical to those reported for $Na_{0.7}TaS_2$.[2,10]

Moreover, partial deintercalation and hydration in water or moist air yielded the same NQI-precession frequency and c-parameter as previously described for the $Na_{0.33}(H_2O)_yTaS_2$ phases[10,11] (Fig. 2, bottom left, Table 1), suggesting that no significant amount of Hg was cointercalated.

compound	a [Å]	c [Å]	ω [Mrad/s]	η	δ [%]	comments
$In_{1.0}TaS_2$ (2H)	3.30	8.75	583	0.0	~1	from $In_{0.17}Ga_{0.83}$
$In_{2/3}TaS_2$ (2H)	3.30	8.00	~480	–	–	"
$In_{1.0}TaS_2$ (2H)	3.30	8.75	581	0.08	~5	from $In_{0.5}Hg_{0.5}$
$Na_{0.7}TaS_2$ (1T)	3.34	7.29	493	0.04	1.5	T=300 K
			518	0.17	2.6	T=77 K
$Na_{0.7}TaS_2$ (2H)	3.32	7.29	424	0.14	3.9	
$Na_x(H_2O)_2TaS_2$ (1T)		11.7	560	0.08	1.0	after subsequent
$Na_{0.33}(H_2O)_2TaS_2$ (2H)		11.7	587	0.00	0.0	hydration

TABLE 1 Lattice parameters, ^{181}Ta-NQI precession frequency (I=5/2), asymmetry parameter η, and line broadening δ of 1T-TaS_2 and 2H-TaS_2 intercalation compounds prepared from liquid eutectics and amalgams.

Na – Intercalation into 1T–TaS_2

In the case of 1T-TaS_2, the contact with the amalgam immediately changed the crystal colour from golden to silver-metallic. At the same time, the characteristic charge density wave (CDW) NQI-signal[12] was replaced by a complicated but discrete frequency distribution (Fig. 2, right top two). Upon further intercalation this frequency distribution became less defined while a frequency component at $\omega \sim 493$ Mrad/s, attributed to the final product, gained more and more intensity. After about a month reaction time the NQI-signal of the final product survived (Fig. 2, middle right) exhibiting axial symmetry and an almost instrumental linewidth (see Table 1).

The precession frequency, the asymmetry parameter (η) and the linewidth increased slightly upon cooling to 77 K (see Table 1); however, not splitting of the NQI-signal due to a possible onset of a CDW-instability was observed.

Partial deintercalation and hydration in moist air or water increased the c-parameter from 7.29Å to 8.8Å, 9.0Å, and finally to 11.8Å, indicating the subsequent uptake of a monolayer and a double layer of water. This, and the fact that TDPAC-spectra of the hydrated samples (Fig. 2, bottom right) exhibited a single precession frequency ($\omega \sim 560$ Mrad/s) only, clearly excludes any significant Hg-cointercalation. However, the TDPAC-spectrum of the hydrated sodium intercalate does not agree with any of the 3R-$Na_x(H_2O)_2TaS_2$-phases[12,13] derived from 1T-TaS_2 (all these phases exhibit a large NQI-splitting due to the presence of a strong CDW), but resembles those of $Na_x(H_2O)_2TaS_2$ derived from 2H-TaS_2 (Fig. 2, bottom, Table 1). Hence, we are led to the conclusion that the sodium intercalation (or the subsequent hydration) induced a Ta-coordination change from octahedral to trigonal-prismatic, as has been previously observed for the chemical lithiation[14].

The slight differences between the NQI-signal of the 1T-TaS_2 and 2H-TaS_2-intercalation products may be explained by a different stacking sequence. In fact, powder diffaction diagrams of the final $Na_{0.7}TaS_2$-products (derived from 1T-TaS_2 and 2H-TaS_2, respectively) were found to be comparable to those reported by W. Omloo *et al.*[2] for α-$Na_{0.7}TaS_2$ and ζ-$Na_{0.7}TaS_2$.

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