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Quaternary pseudo-intercalation phases T_x $[Nb_2S_2C]$ ($T \equiv V$, Cr, Mn, Fe, Co, Ni, Cu) and metastable Nb_2S_2C formed by topochemical synthesis*

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Abstract

The title phases are prepared by topochemical reaction starting with Nb_2SC. They are isotypic with the corresponding intercalation compounds of Ta_2S_2C. Nb_2S_2C is formed by deintercalation of $Cu_{0.7}[Nb_2S_2C]$. It is isotypic to 1T–Ta_2S_2C. The magnetic properties are determined.

1. Introduction

Ta_2S_2C and Ta_2Se_2C are interesting layer compounds [1, 2]. However an analogous phase with niobium cannot be prepared by direct synthesis. The H-phase Nb_2SC_{1-x} [3, 4] is the only ternary compound in the Nb–S–C system. Ta_2S_2C is a versatile host lattice for intercalation [5–7], the intercalation phases with the first row transition metals titanium to copper being the most stable. This observation prompted us to try the synthesis of the analogous quaternary compounds with niobium.

2. Syntheses

As it is very difficult to equilibrate multicomponent samples of the heavier transition elements at temperatures around 1000 °C, mixtures of $Nb_2SC_{0.98}$ with sulfur and the respective transition metal powder were chosen as starting materials. The crystal structure of Nb_2SC is built up by a close packed stacking of hexagonal layers with sequence ..NbCNbSNbC... while the presumptive structure of T_x $[Nb_2S_2C]$ should have the stacking sequence ..NbCNbSTSNbC... The synthesis of the quaternary phases can thus be

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*Dedicated to Professor W. Bronger and Professor Ch. J. Raub on the occasions of their 60th birthdays.

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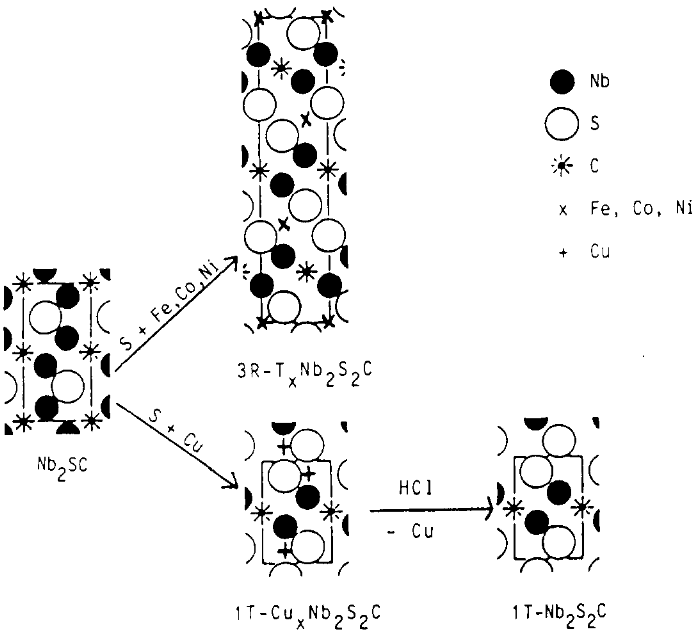

Fig. 1. Topochemical reaction scheme of the formation of T_x [Nb_2S_2C] phases and Nb_2S_2C ((110) sections through the unit cells).

visualized by insertion of an additional sulfur layer and the transition metal into the lattice of the H-phases (Fig. 1).

The phases were formed by heating the reaction mixtures to 1000–1200 °C for 48 h in sealed silica tubes. The phases with chromium, iron metals and copper form most readily. In the case of vanadium and manganese a second heat treatment was necessary. With titanium no synthesis was successful.

The products were fine, polycrystalline, black-gray powders in all cases. They were stable in air, with the exception of the copper compound which was partially deintercalated by slow oxidation (*vide infra*).

3. Phase analyses and crystal structures

All materials were investigated by Guinier photographs. The lattice parameters were refined by the computer program GITTER [8].

It was difficult to determine exactly the ranges of existence with respect to the T element because of the very small dependence of the lattice parameters on x. An average range of $0.35 \leqslant x \leqslant 0.7$ is estimated for T = V to Ni, while x is about 0.7 for Cu_x [Nb_2S_2C], prepared by high temperature synthesis.

The powder diagrams of the phases with T = V to Ni could be indexed with a triple primitive hexagonal unit cell indicating a 3R stacking of the Nb_2S_2C partial lattice with the T-metal situated in octahedral sites of the

Van der Waals gap. However, Cu_x $[Nb_2S_2C]$ has a primitive hexagonal cell corresponding to a 1T stacking, copper being tetrahedrally coordinated by sulfur. The two crystal structures observed are analogous to those of the T_x $[Ta_2S_2C]$ phases. In Table 1 the lattice parameters are compiled; in Tables 2 and 3 intensity calculations for $Cr_{0.5}$ $[Nb_2S_2C]$ and $Cu_{0.7}$ $[Nb_2S_2C]$ are presented.

TABLE 1

Lattice parameters and magnetic data of T_x $[Nb_2S_2C]$ phases

	a (Å)	c (Å)	μ_{eff} (μ_B)	$\chi_{TIP} \times 10^{-4}$ ($cm^3\ mol^{-1}$)	ϑ_p (K)
$V_{0.6}$ $[Nb_2S_2C]$	3.294	25.76	1.0	1.8	3
$Cr_{0.6}$ $[Nb_2S_2C]$	3.306	25.62	2.4	6.2	−45
$Mn_{0.5}$ $[Nb_2S_2C]$	3.306	25.97	5.3	2.7	−40
$Fe_{0.5}$ $[Nb_2S_2C]$	3.303	25.83	4.9	0	33
$Co_{0.5}$ $[Nb_2S_2C]$	3.305	25.11	1.7	1.0	30
$Ni_{0.5}$ $[Nb_2S_2C]$	3.303	25.33	0.8	5.2	33
$Cu_{0.7}$ $[Nb_2S_2C]$	3.310	9.03	0	1.2	–
Nb_2S_2C	3.27	8.56	0	0	–

χ_{TIP}, temperature independent peremepnelism; ϑ_p, peremepnetic Curie temperature.

TABLE 2

Powder diagram of 3R–$V_{0.5}$ $[Nb_2S_2C]$ (Cu $K\alpha_1$)

hkl	d_{obs}	I_{obs}	I_{calc}	hkl	d_{obs}	I_{obs}	I_{calc}
(003)	8.5692	vst	100	(119)	1.4306	mw	14
(006)	(4.2883)*	–	0	(00.18)	1.4301		4
(009)	2.8598	w	12	(021)	1.4282	w	12
(101)	2.8421	st	74	(202)	(1.4215)*	–	0
(012)	(2.7923)*	–	2	(10.16)	1.4030	mw	15
(104)	2.6160	m	35	(024)	1.3955	w	8
(015)	2.4996	st	92	(205)	1.3783	mw	18
(107)	2.2578	st	85	(01.17)	1.3396	w	17
(00.12)	2.1430	mw	23	(027)	1.3334	mw	21
(018)	2.1380	vst	95	(11.12)	1.3077	st	40
(10.10)	1.9129	w	8	(208)			26
(01.11)	(1.8108)*	–	2	(02.10)	(1.2501)*	–	3
(00.15)	1.7177	vw	7	(00.21)	(1.2252)*	–	2
(110)	1.6534	mst	74	(10.19)	(1.2240)*	–	5
(10.13)	1.6285	m	28	(20.11)	(1.2202)*	–	1
(113)	1.6226	w	11	(11.15)	1.1886	mw	17
(01.14)	(1.5462)*	–	2	(01.20)	1.1727	mw	17
(116)	(1.5412)*	–	0	(02.13)	1.1589	w	13

*Unobserved, d-value calculated.

m, medium; mw, medium weak; mst, medium strong; st, strong; vst, very strong; w, weak; vw, very weak.

R3m, V in 3b; Nb in 6c, $z_{Nb} = 0.377$; S in 6c, $z_S = 0.220$; C in 3a.

TABLE 3

Powder diagram of 1T–$Cu_{0.7}$ [Nb_2S_2C] (Cu $K\alpha_1$)

$h\,k\,l$	d_{obs}	I_{obs}	I_{calc}	$h\,k\,l$	d_{obs}	I_{obs}	I_{calc}
(001)	8.9596	st	59	(105)	1.5287	mw	10
(002)	(4.5150)*	–	0	(006)	1.4970	vw	0.4
(003)	3.0070	m	6	(113)	1.4509	w d**	7
(100)	2.8726	st	49	(200)	1.4359	m	8
(101)	2.7338	mst	30	(201)	1.4175	w d	6
(102)	2.4213	vst	100	(202)	1.3690	st	22
(004)	2.2565	m	15	(114)	1.3350	st d	22
(103)	2.0758	st	64	(106)			18
(005)	1.8064	mw	6	(203)	1.2950	m	18
(104)	1.7753	m	30	(007)	1.2940	vw	4
(110)	1.6572	vst	53	(115)	1.2202	m	13
(111)	1.6302	mw	6	(204)	1.2100	mw	11
(112)	(1.5539)*	–	0	(107)	1.1760	m	14

*Unobserved, *d*-value calculated.

**diffuse.

Abbreviations as defined in Table 2.

$P3m1$, all atoms in 2d: $z_{Cu}=0.440$; $z_{Nb}=0.127$; $z_S=0.682$.

4. Metastable Nb_2S_2C

Copper can be deintercalated by treating Cu_x [Nb_2S_2C] either with concentrated hydrochloric acid or with iodine in acetonitrile. A two-step treatment is necessary to completely remove the copper. The deintercalation is indicated by a dramatic decrease of the *c* axis (Table 1) accompanied by a line broadening in the powder diagrams indicating stacking disorder. We did not succeed in deintercalating the 3R-phases.

5. Magnetic properties

The magnetic susceptibilities were measured with the SUS 10 Faraday Magnetometer [9] in the range 80–550 K. At room temperature all samples are paramagnetic. The temperature dependence of the susceptibilities obeys a Curie–Weiss law augmented by a temperature independent term. The magnetic parameters are given in Table 1. Fe_x [Nb_2S_2C] samples show a more complex behavior, with a Néel-point like maximum between 190 and 346 K ($x=0.4$ and 0.6 respectively). The concentration dependence of this maximum allows us to locate the iron rich phase boundary close to $x=0.6$ (Fig. 2).

The magnetic susceptibilities of $Cu_{0.7}$ [Nb_2S_2C] are very small ($\chi_g=4\times10^{-7}$ cm^3 g^{-1}) and almost temperature independent. On deintercalation of copper the susceptibilities are reduced to values of $\pm5\times10^{-8}$ cm^3 g^{-1} (≈0).

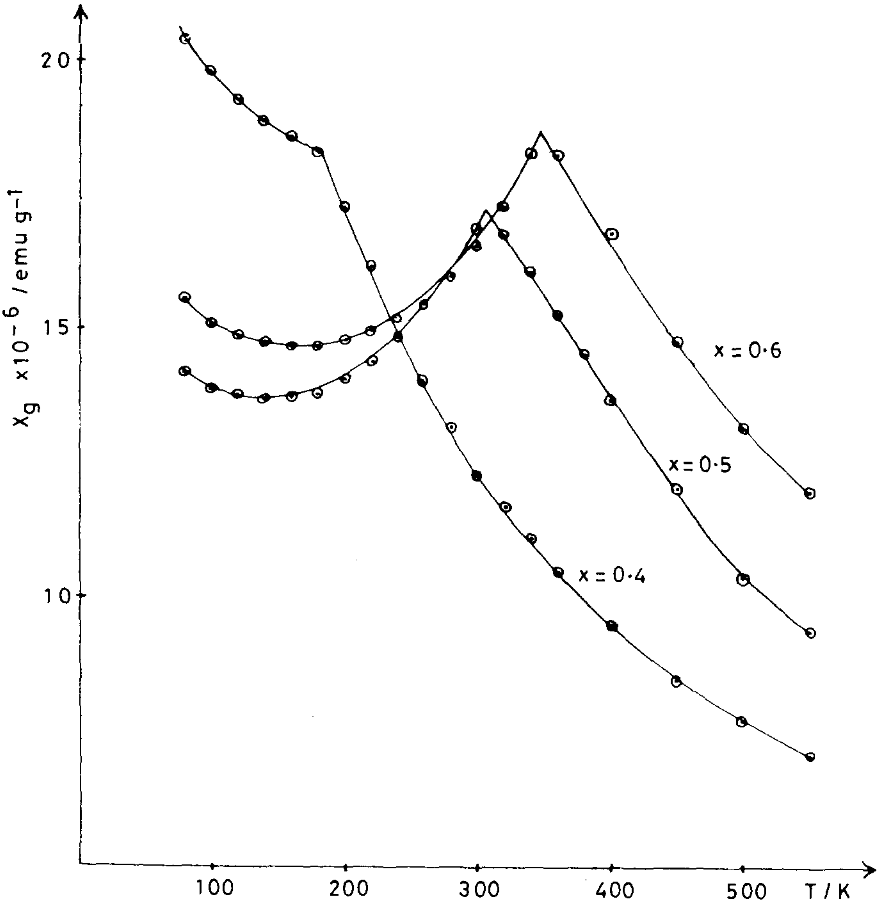

Fig. 2. Temperature dependence of the magnetic susceptibilities of Fe_x [Nb_2S_2C] phases.

6. Discussion

The structural features of the above described phases are very similar to those of the T_x [Ta_2S_2C] intercalation compounds. The maximum degree of intercalation, however, is about twice in the 3R–T_x [Nb_2S_2C] phases.

The interlayer distance in the Van der Waals gap of the Nb_2S_2C host lattice in 1T–$Cu_{0.7}$ [Nb_2S_2C] is ≈0.5 Å larger than in the 3R-phases. This fact explains why the 1T-phase can be deintercalated by soft chemical methods and the 3R-phases cannot.

The magnetic moments vary in a smooth fashion from vanadium to copper with a maximum for manganese and iron. The values of the moments, however, are smaller than the appropriate spin-only moments. This observation, together with the relatively high temperature independent paramagnetism χ_{TIP} of the 3R-phases, suggests a partially delocalized, metallic type of bonding. The main contribution to paramagnetism, including the temperature independent part, comes from the 3d transition elements. This is indicated by the rather low paramagnetism of 1T–$Cu_{0.7}$ [Nb_2S_2C], compatible with Cu(I), and the even lower one of deintercalated Nb_2S_2C ($\chi_g \approx 0$).

The Fe_x [Nb_2S_2C] phases show an interesting magnetic behavior (Fig. 2) which might indicate antiferromagnetism. In this case, however, magnetic ordering would occur between iron-bearing layers separated by 8.6 Å. A neutron diffraction study is in progress.

We suggest the term "pseudo-intercalation" phase for ternary or higher-component compounds being structurally or chemically closely related to intercalation phases, although the host lattice alone does not exist as a thermodynamically stable compound. Apart from the crystal structure typical chemical properties of intercalation phases are non-stoichiometry with respect to the intercalate, and in many cases mobility and reactivity of the intercalate species, often accompanied by redox phenomena of the host lattice. Besides the title compounds several other chalcogenide phases of this kind are known, *e.g.* layered phases M_xVS_2 [10], M_xCrS_2 [11, 12] or Chevel phases. In some cases the metastable host lattice can be isolated by soft chemical deintercalation, *e.g.* Nb_2S_2C, VS_2 [13], $CrSe_2$ [14] or Mo_3S_4 [15].

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