## Preparation, Crystal Structure, and Magnetic Properties of $\beta$ -Li<sub>3</sub>TiF<sub>6</sub> = Li<sub>2</sub><sup>[4]</sup>Li<sub>7</sub><sup>[6]</sup>(TiF<sub>6</sub>)(TiF<sub>6</sub>)<sub>2</sub> – a Double Fluoride?

Avesh K. Tyagi<sup>1</sup>), Rainer Pöttgen and Jürgen Köhler\*

Stuttgart, Max-Planck-Institut für Festkörperforschung

Received February 12th, 1996.

Professor Hans Georg von Schnering zum 65. Geburtstag gewidmet

**Abstract.** Purple colored single crystals of the  $\beta$ -modification of Li<sub>3</sub>TiF<sub>6</sub> have been prepared by heating an appropriate mixture of LiF and TiF<sub>3</sub> at 820 °C under an argon atmosphere.  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub> crystallizes in C2/c with a = 14.452(2) Å, b = 8.798(1) Å, c = 10.113(1) Å and  $\beta$  = 96.30(1)°. The structure is isotypic to  $\beta$ -Li<sub>3</sub>VF<sub>6</sub> and contains isolated compressed TiF<sub>6</sub> octahedra (d<sub>Ti-F</sub> = 1.91-2.01 Å). Magnetic properties of  $\beta$ -  $Li_3TiF_6$  were studied and discussed. Band structure calculations and calculations of the Madelung part of the lattice energy, MAPLE, were performed to discuss the chemical bonding.

**Keywords:**  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub>; crystal structure; band structure; Jahn Teller effect; magnetism

# Darstellung, Kristallstruktur und magnetische Eigenschaften von $\beta$ -Li<sub>3</sub>TiF<sub>6</sub> = Li<sub>2</sub><sup>[4]</sup>Li<sub>7</sub><sup>[6]</sup>(TiF<sub>6</sub>)(TiF<sub>6</sub>)<sub>2</sub> – ein Doppelfluorid?

**Inhaltsübersicht.** Purpurfarbene Einkristalle von  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub> wurden durch Erhitzen eines Gemenges von LiF und TiF<sub>3</sub> (3:1) bei 820 °C unter Argon erhalten.  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub> kristallisiert in C2/c mit a = 14.452(2) Å, b = 8.798(1) Å, c = 10.113(1) Å und  $\beta$  = 96.30(1)°. Die Struktur ist isotyp mit  $\beta$ -Li<sub>3</sub>VF<sub>6</sub> und ent-

### Introduction

Fluorotitanates(III) are of interest for their structural, magnetic, electronic and optical properties. Because of the d<sup>1</sup> configuration of Ti<sup>3+</sup> Jahn-Teller effects can always be expected in these compounds. The binary fluoride TiF<sub>3</sub> [1, 2] is known for a long time, but only a few fluorotitanates(III), like A<sub>3</sub>TiF<sub>6</sub> (A = Li, Na, K), have been characterized [3]. *Hoppe* et al. succeeded in preparing single crystals of fluorotitanates(III) such as  $Cs_2NaTiF_6$ ,  $Cs_2KTiF_6$ ,  $Rb_2KTiF_6$  [4, 5]. According to Xray powder diffraction data Li<sub>3</sub>TiF<sub>6</sub> occurs, like other Li<sub>3</sub>MF<sub>6</sub> (M = Al, Ga, V, Cr and Fe) compounds, in two modifications [6]. The  $\alpha$ -form (orthorhombic) can be obtained only by quenching a corresponding sample from 600 – 800 °C to room temperature. Slow cooling, which is hält isolierte gestauchte TiF<sub>6</sub>-Oktaeder ( $d_{Ti-F} = 1.91 - 2.01$  Å). Die magnetischen Eigenschaften von  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub> untersucht und diskutiert. Die Bindungsverhältnisse werden anhand von Bandstruktur Rechnungen und Berechnungen des Madelunganteils der Gitterenergie, MAPLE, diskutiert.

necessary for obtaining single crystals, always leads to the  $\beta$ -form. Herein, we report on the preparation, structure refinement on the basis of single crystal data and magnetic studies of  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub>.

#### Experimental

LiF (Merck, 99.9%) was used as starting material. TiF<sub>3</sub> was prepared by the reaction of TiH<sub>2</sub> (Alfa, 99%) and HF at 700 °C. It was analyzed for oxygen impurity by a "NO" series of analyzer coupled with "BINOS" Infrared gas analyzer. The oxygen content was found to be negligible (<0.1 wt %). LiF and TiF<sub>3</sub> were first vacuum (~10<sup>-4</sup> torr) dried at 300 °C for 24 hours. An intimate mixture of LiF and TiF<sub>3</sub> in 3:1 molar ratio was prepared in a dry box and pressed into a pellet. The pellet was transferred to a platinum tube and then placed in a quartz glass tube. Platinum was used to avoid the contact of fluorides with the quartz glass surface. First, this quartz glass tube was evacuated to a pressure of ~10<sup>-5</sup> torr and subsequently filled with argon and sealed on-line. It was heated at

<sup>&</sup>lt;sup>1</sup>) Permanent address: Applied Chemistry Division, Bhabha Atomic Research Centre Trombay, Bombay (400 085), India

820 °C for 19 hours and subsequently cooled to room temperature. The color of the product was purple, which is characteristic for Ti(III)fluorides. Powder samples of  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub> were found to be slightly sensitive to air and moisture.

An X-ray powder pattern was recorded with Cu-K $\alpha$  radiation on a Stoe-STADI diffractometer with a position sensitive detector. The radiation was Cu-K $\alpha$  monochromatized using a curved graphite crystal. The powder pattern was recorded from  $2\theta = 10^{\circ}$  to 90° and was indexed on the basis of a monoclinic unit cell with a = 14.452(2) Å, b = 8.798(1) Å, c = 10.113(1) Å, and  $\beta = 96.30(1)^{\circ}$ . The powder data along with the indices and d spacings are given in Table 1.

**Table 1** X-ray powder data and indexing for  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub>

d <sub>obs</sub>	$\mathbf{d}_{cal}$	h k 1	$Int_{obs}$	$Int_{cal}$
4.3970	4.3987	02 0	30.0	<b>32.</b> 1
4.2892	4.2904	11- <b>2</b>	60.0	60.1
4.2045	4.2060	310	100.0	100.0
3.9215	3.9223	20 2	40.0	35.9
3.0862	3.0857	40 - 2	40.0	44.4
2.9273	2.9275	22 2	40.0	36.5
2.5262	2.5261	42 - 2	15.0	14.5
2.5006	2.5008	33 0	15.0	14.7
2.3943	2.3944	60 0	15.0	14.1

**Table 2** Crystal data and structure refinement for  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub>

Empirical formula	Li₃TiF <sub>6</sub>
Formula weight [g/mol]	182.7
Temperature [K]	293(2)
Wavelength [pm]	71.073
Crystal system	monoclinic
Space group; Z	C2/c (No. 15); 12
Unit cell dimensions [Å],	a = 14.452(2), (14.422(3))
powder data, (single crystal	b = 8.798(1), (8.756(2))
data)	c = 10.113(1), (10.070(2))
,	$\beta = 96.30(1)^{\circ}, (96.32(3)^{\circ})$
	V = 1278.2
Calculated density [g/cm <sup>3</sup> ]	2.865
Crystal size [mm]	0.1×0.1×0.01
Absorption coefficient [mm <sup>-1</sup> ]	19.31
Diffractometer type	Stoe image plate (IPDS)
Detector distance	50 mm
Exposure time	4 minutes per plate
$\varphi$ range, increment	0-150°, 0.8°
Movement mode	oscillation
F(000)	1020
$2\theta$ range for data collection	12° to 56°
Range in hkl	$-20 \le h \le 20, -12 k \le 12,$
	$-14 \le l \le 12$
Total no. reflections	5536
Independent reflections	$1834 (R_{int} = 0.039)$
Reflections with $I > 2\sigma(I)$	1161 ( $R_{sigma} = 0.028$ )
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	1834/0/141
Goodness-of-fit on F <sup>2</sup>	1.131
R (aniso)	0.039 for 1161 reflections
	$(I > 2\sigma(I))$
R <sub>w</sub> (aniso)	0.022 for 1161 reflections
	$(I > 2\sigma(I))$
Extinction coefficient	0.001(1)

**Table 3** Atomic parameters for  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub>

atom	site	x	у	Z
Li1	4e	0	0.1946(6)	0.25
Li2	8f	0.2981(2)	0.3560(4)	0.5705(4)
Li3	8 f	0.3303(2)	0.2085(5)	0.9521(4)
Li4	8 f	0.0196(3)	0.3507(4)	0.5268(4)
Li5	8 f	0.1405(3)	0.8473(4)	0.2734(4)
Ti1	4a	0	0	0
Ti2	8f	0.3384(1)	0.0021(1)	0.7086(1)
<b>F</b> 1	8 f	0.0910(1)	0.3373(1)	0.1872(1)
F2	8 f	0.2316(1)	0.3347(1)	0.8866(1)
F3	8 f	0.0987(1)	0.3390(1)	0.6881(1)
F4	8 f	0.2475(1)	0.0205(1)	0.8444(1)
F5	8 f	0.0772(1)	0.1672(1)	0.9378(1)
F6	8f	0.9266(1)	0.1678(1)	0.0708(1)
F7	8 f	0.4216(1)	0.9910(1)	0.5668(1)
F8	8 f	0.2603(1)	0.1558(1)	0.6085(1)
F9	8 f	0.0739(1)	0.0018(1)	0.1680(1)

Single crystals were selected from the reaction product by mechanical fragmentation. They were characterized with a Buerger precession camera in order to establish both symmetry and suitability for intensity data collection. Intensity data were collected by a Stoe Image Plate Diffractometer System (IPDS) using graphite monochromatized Mo-K $\alpha$  radiation. Details of the data collection are given in Table 2. The structure, which is isotypic to  $\beta$ -Li<sub>3</sub>VF<sub>6</sub> [7], was refined with the program SHELX [8] with anisotropic displacement for all atoms. According to the refinement of the structure the space group was found to be C2/c. A final difference Fourier synthesis revealed no significant residual peaks. Listings of the anisotropic displacement parameters and structure factor tables are available<sup>2</sup>). The atomic positions and anisotropic displacement parameters are given in Table 3 and 4, respectively.

Magnetic data were obtained in the temperature range 6 to 320 K using a SQUID magnetometer (Quantum Design) at an external magnetic flux density of 1 T.

## Discussion

 $\beta$ -Li<sub>3</sub>TiF<sub>6</sub> is isotypic to  $\beta$ -Li<sub>3</sub>VF<sub>6</sub> [7]. According to Li(1)Li(2)<sub>2</sub>Li(3)<sub>2</sub>Li(4)<sub>2</sub>Li(5)<sub>2</sub>Ti(1)Ti(2)<sub>2</sub>F<sub>18</sub> the structure contains five different Li and two different Ti. Motifs of the mutual adjunction [9] together with ECoN values [10] are given in Table 5 and interatomic distances in Table 6. The distances and angles within the TiF<sub>6</sub> octahedra in  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub> are given together with the corresponding connection with neighbouring LiF<sub>n</sub> polyhedra by the *Schlegel* diagrams and *Schlegel* projections [11] in Fig. 1.

A projection of the structure of  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub> is shown in Fig. 2. It can be described in terms of a cubic close packing of F along [001], in which Ti(1) and Ti(2) occupy 1/6

<sup>&</sup>lt;sup>2</sup>) Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405346, the names of the authors, and the journal citation.

atom	U11	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	$U_{13}$	$\mathbf{U}_{12}$	
Li1	0.025(3)	0.024(3)	0.021(3)	0	0.0020(20)	0	
Li2	0.013(2)	0.021(2)	0.025(2)	-0.0022(15)	0.0018(14)	0.0012(13)	
Li3	0.017(2)	0.033(2)	0.021(2)	-0.0010(20)	0.0012(14)	0.0034(15)	
Li4	0.021(2)	0.019(2)	0.029(2)	-0.0010(20)	0.0040(20)	0.0001(15)	
Li5	0.022(2)	0.019(2)	0.023(2)	-0.0005(14)	0.0005(15)	-0.0019(14)	
Ti1	0.0116(3)	0.0112(3)	0.0122(3)	-0.0002(2)	0.0018(2)	-0.0007(2)	
Ti2	0.0113(3)	0.0101(3)	0.0117(3)	-0.0003(9)	0.0023(2)	0.0002(1)	
F1	0.0187(6)	0.0158(6)	0.0183(6)	-0.0032(5)	0.0051(5)	-0.0039(5)	
F2	0.0162(6)	0.0172(6)	0.0179(7)	0.0045(5)	0.0024(5)	0.0045(5)	
F3	0.0202(6)	0.0150(6)	0.0164(6)	-0.0017(5)	-0.0019(5)	-0.0022(4)	
F4	0.0165(6)	0.0174(6)	0.0166(7)	0.0013(5)	0.0068(5)	0.0005(4)	
F5	0.0177(6)	0.0168(6)	0.0169(6)	0.0001(5)	0.0037(5)	-0.0057(5)	
F6	0.0136(6)	0.0147(6)	0.0179(7)	-0.0022(5)	0.0022(5)	0.0025(4)	
F7	0.0181(7)	0.0171(7)	0.0194(7)	0.0010(4)	0.0086(5)	0.0020(4)	
F8	0.0185(6)	0.0153(6)	0.0182(7)	0.0034(5)	-0.0006(5)	0.0021(5)	
F9	0.0193(7)	0.0193(7)	0.0177(7)	0.0004(4)	-0.0029(6)	0.0004(4)	

**Table 4** Anisotropic displacement parameters (pm<sup>2</sup>) for  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub>

**Table 5** Motifs of mutual adjunction [9], coordination numbers (CN) and ECoN values [10] for  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub>

atom	2F1	2F2	2F3	2F4	2F5	2F6	2F7	2F8	2F9	CN	ECoN
Ti1	_	_	_	_	2/1	2/1	_	_	2/1	6	5.9
2Ti2	1/1	1/1	1/1	1/1	_	_	1/1	1/1	_	6	6.0
1Li1	2/1	_	_	_	_	2/1	_	_	2/1	6	5.5
2Li2	_	_	_	1/1	_	1/1	_	2/2	_	4	4.0
2Li3	1/1	2/2	_	1/1	1/1	_	(1/1)	—	-	5 + 1	4.7
2Li4	(1/1)	_	1/1	_	1/1	1/1	2/2		_	5 + 1	4.6
2Li5	_	1/1	1/1	1/1	1/1	_	_	(1/1)	1/1	5 + 1	4.5
CN	3 + 1	4	3	4	4	4	<b>3</b> + 1	<b>3</b> + 1	3		
ECoN	3.1	3.3	3.0	3.4	3.8	3.8	3.2	3.0	2.6		

**Table 6** Interatomic distances (Å) in  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub>

Ti1—F9	1.905×2	Ti2—F3	1.941
F5	$1.990 \times 2$	F8	1.969
F6	1.996×2	F7	1.972
		F2	1.976
Li1—F1	1.973×2	<b>F</b> 1	1.978
F6	$2.011 \times 2$	F4	2.008
F9	$2.214 \times 2$		
		Li4—F3	1.889
Li3F2	1.870	F7	1.932
<b>F</b> 1	1 <b>.947</b>	F7	1.954
F5	1.974	F6	2.082
F2	1.981	F5	2.191
F4	2.251	<b>F</b> 1	2.548
<b>F7</b>	2.415		
		Li5—F3	1.919
Li2—F4	1.842	F9	1.920
F6	1.869	F5	1.988
F8	1.896	F4	2.004
F8	1.914	F2	2.297
		F8	2.532



**Fig. 1** Schlegel projections and Schlegel diagrams [11] of a  $Ti(1)F_6$  octahedron (a and c) and a  $Ti(2)F_6$  octahedron (b and d) in  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub>. In (c) and (d) the Ti—F distances (pm) are given at the terminal positions. The F—F distances and their corresponding angles with respect to the central atom (not included) are indicated next to the edges. Vertex-sharing and edge-sharing with LiF<sub>n</sub> polyhedra are given in (a) and (b).



Fig. 2 Projection of the structure of  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub>. Small black circles represent F and open circles Li. TiF<sub>6</sub> octahedra are drawn.



Fig. 3 Projection of a sheet containing  $Li(1)F_6$  and  $Li(4)F_6$  octahedra along [001] in  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub>. Ti(1)—F bonds are emphasized.



**Fig. 4** Projection of a sheet containing  $\text{Li}(5)\text{F}_6$  and  $\text{Li}(3)\text{F}_6$  octahedra together with  $\text{Li}(2)\text{F}_4$  tetrahedra along [001] in  $\beta$ - $\text{Li}_3\text{Ti}\text{F}_6$ . Ti(2)—F bonds are emphasized.

of the octahedral voids in such a way that only isolated  $TiF_6$  octahedra are present. A comparable arrangement of octahedra is not known from binary MX<sub>6</sub> type compounds. Within double sheets of F two third of the octahedral voids are occupied by Li(1), Li(4) and Ti(1), see Fig. 3. These sheets alternate with two comparable sheets containing Ti(2), Li(3) and Li(5), which occupy 1/2 of the octahedral voids, see Fig. 4. 1/12 of the tetrahedral voids are occupied by Li(2). So, altogether 5/9 of the octahedral and 1/9 of the tetrahedral voids are occupied. In the structure of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> [12] one half of the Ga is octahedrally and the other half is tetrahedrally coordinated by O, which are in a close packed arrangement<sup>3</sup>). The question arises, whether there is a systematic concerning the ratio of occupied tetrahedral and octahedral holes and the kind of metals in compounds of the type  $M_2X_3$ (M = metal, X = O, F).

The description of the structure of  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub> given above is rather rough. In fact, only for Li(1) and Li(2) the coordination numbers agree approximately with the calculated ECoN values (see Table 4). The ECoN values for Li(3), Li(4) and Li(5) are significantly lower indicating that each of these atoms is surrounded by 5 nearest F and one additional F(7), F(1) and F(8), respectively, which have distances to Li ranging from 2.42 to 2.53 Å. Therefore, the coordination numbers of Li(3), Li(4) and Li(5) are described as 5 + 1. As a consequence, the coordination numbers of F(1), F(7) and F(8) are 3 + 1. The remaining F are trigonally or distorted tetrahedrally coordinated (see Table 4).

It is known that the  $d^1$  configuration of  $Ti^{3+}$  calls for a Jahn-Teller distortion (relatively weak) of octahedral  $TiX_6^{3-}$  molecules. A similar effect can be expected in solids, however, distortions of MX<sub>6</sub> octahedra are often already caused by next nearest neighbours connecting these octahedra to a three-dimensional network. As an example, the Al—F distances within the  $AlF_6$  octahedra in  $\alpha$ -Li<sub>3</sub>AlF<sub>6</sub> range from 1.79 to 1.83 Å [13]. A similar situation is found for the TiF<sub>6</sub> octahedra in  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub>, see Figure 4. Both, the  $Ti(1)F_6$  and  $Ti(2)F_6$  octahedra have Ti-F distances between 1.91 and 2.01 Å and are compressed along a F-Ti-F axis. All F-F edges, which are shared between TiF<sub>6</sub> octahedra and LiF<sub>n</sub> polyhedra are short (2.62 Å to 2.70 Å) compared to the others (2.80 Å to 2.93 Å), i.e. the distortions of the TiF<sub>6</sub> octahedra are as expected from the mode of connection with the adjoining polyhedra around Li. It may be added here that a significantly stronger compression has been found for the isoelectronic  $VF_6$  octahedra in  $VF_4$  [14] with V—F distances of 1.70 Å (2×) and 1.92 Å (4×), where the  $VF_6$  octahedra are connected to sheets via four corners. A comparison with distortions of the AlF<sub>6</sub> octahedra in  $\beta$ -Li<sub>3</sub>AlF<sub>6</sub> or GaF<sub>6</sub> octahedra in  $\beta$ -Li<sub>3</sub>GaF<sub>6</sub>

<sup>&</sup>lt;sup>3</sup>) MgTiO<sub>3</sub> and LiNbO<sub>3</sub> are further examples with a metal/anion ratio of 2/3 and metal-anion distances of approximately 2.0 Å.

would be desirable, but unfortunately their structures are not yet known.

Band structure calculations on the basis of the Extended Hückel method [15-21] have been performed, see Figure 5. The HOCO (highest occupied crystal orbital) in  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub> at about -9.2 eV is mostly Ti centered. The COOP curves indicate that for the Ti(1)F<sub>6</sub> octahedron



Fig. 5 a) Total density of states (DOS) together with the Projection for the Ti atoms (black). COOP curves for the Ti(1)—F interactions (b) and the Ti(2)—F interactions (c).



**Fig. 6** a) Highest occupied molecular orbitals (HOMO) for a) the Ti(1)F<sub>6</sub> octahedron (pointgroup i) and b) the Ti(2)F<sub>6</sub> octahedron (pointgroup 1) in  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub>. The HOMO for the comparable V(1)F<sub>6</sub> (c) and the V(2)F<sub>6</sub> octahedron (d) in  $\beta$ -Li<sub>3</sub>VF<sub>6</sub> are also given. The surface value of the wave functions has been set to 0.06 in all four cases.



Fig. 7 Schlegel projections [11] of a V(1)F<sub>6</sub> octahedron (a) and a V(2)F<sub>6</sub> octahedron (b) in  $\beta$ -Li<sub>3</sub>VF<sub>6</sub>, see Figure 1.

only Ti(1)—F(5) and Ti(1)—F(6) antibonding states are partially occupied, whereas the Ti(1)-F(9) states lie above the Fermi level. A similar situation is found for the  $Ti(2)F_6$  octahedron. In this case all Ti-F antibonding states are partially occupied, although it can be seen that the bonds with short distances (Ti(2)-F(3)) and Ti(2)—F(8)) exhibit the smallest contribution. A special analysis [22, 23] of the octahedral molecular  $TiF_{6}^{3-}$ units in  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub> leads to the corresponding contour plots of the wave functions in Fig. 6 and confirm the picture given above. There is considerable d character in the molecular orbitals below the Fermi level. Specially, we find the Ti(1) contribution to consist of mostly  $d_{x2-y2}$ having fair overlap with the F(4) p and F(8) p hybrids. For the  $Ti(2)F_6$  octahedron we find the Ti(2) contribution as a mixing of  $d_{x2-y2}$  and  $d_{z2}$  and also overlap with the p hybrids of four F of a basal plane and nearly no contribution from F(3) and F(9). Because of the  $d^2$  configuration of  $V^{3+}$  it seemed interesting to analyze the situation for  $\beta$ -Li<sub>3</sub>VF<sub>6</sub>, where the V—F distances within the  $V(1)F_6$  and  $V(2)F_6$  octahedra lie between 1.90 and 1.97 Å and the compressions of the octahedra are nearly identical to those found for the  $Ti(1)F_6$  and  $Ti(2)F_6$  octahedra in  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub>, see Figure 7. For the V(1)F<sub>6</sub> octahedron there is no significant difference to the Ti analogue, see Figure 5c). However, the character of the HOMO of the less compressed  $V(2)F_6$  octahedron is mainly  $d_{x2-y2}$ , but with significant contributions of  $d_{z2}$ ,  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  and differs strongly from the HOMO of the  $Ti(2)F_6$  octahedron, see Figure 5 d). For a deeper insight magnetic and optical properties of  $\beta$ -Li<sub>3</sub>VF<sub>6</sub> have to be measured.

**Table 7** Contribution of the atoms to the Madelung part, of the lattice energy, MAPLE, [22, 23] [kcal/mol] for  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub>

atom	MAPLE	atom	MAPLE	
	kcai/moi		kcai/moi	
Li1	152.1	F2	147.5	
Li2	154.3	F3	146.4	
Li3	153.4	F4	148.7	
Li4	154.7	F5	146.4	
Li5	155.0	F6	152.7	
Ti1	1005.3	F7	147.0	
Ti2	1004.9	F8	149.4	
F1	145.8	F9	143.4	

Madelung part of the lattice energy (kcal/mol):  $\Sigma 2352.4$ 

For an electrostatic analysis we have calculated MAPLE [23, 24] (Madelung Part of Lattice Energy) for  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub> and compared these values with MAPLE for the binary fluorides LiF (288 kcal/mol) and TiF<sub>3</sub> (1510 kcal/mol), see Table 7. According to

3×MAPLE(LiF)	+	MAPLE(TiF <sub>3</sub> )	=	MAPLE( $Li_{3}TiF_{6}$ )
3×288	+	1510	=	2374 kcal/mol

the sum of MAPLE values for the binary fluorides is only 0.9% higher than the calculated value of 2352 kcal/mol for  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub> and is in good agreement with the structure refinement, especially with respect to the determined positions of the Li.



Fig. 8 Reciprocal magnetic susceptibility vs temperature for  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub>

The magnetisation of a sample of  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub> was measured between 6 and 320 K at magnetic flux density of 1 T. The reciprocal magnetic susceptibility,  $1/\chi$ , calculated from these data is shown in Fig. 8. It shows a slight deviation from the linearity at about 150 K. For a comparison with other structures we applied the Curie-Weiss law to the high temperature part and the extrapolation led  $\mu = 1.83 \mu_B$ . This value is in good agreement with the observed magnetic moments for Cs<sub>2</sub>KTiF<sub>6</sub> and TiF<sub>3</sub> [5], which have been calculated in a similar way, but exceeds the spin-only value of  $\mu_{eff} = 1.73 \mu_B$  for Ti<sup>3+</sup>. Such discrepancies have been attributed to distortions of the TiX<sub>6</sub> octahedra, which split the <sup>2</sup>T<sub>2g</sub> ground term [25, 26].

The magnetic data can also be fitted on the basis of the modified Curie-Weiss law  $\chi_{mol} = C/T + \chi_o$ , where  $\chi_o$  is a temperature independent part of the susceptibility. Then a rather low value of  $\mu_{eff} = 1.44 \,\mu_B$  is obtained, which can be attributed to spin-orbit coupling. The oxygen content of the sample was found to be negligible (<0.5 wt %) and hence the possibility of getting a low value of  $\mu_{eff}$  due to the presence of Ti<sup>4+</sup> is completely ruled out.

More detailed investigations about the magnetic properties are necessary and may be obtained by measurements on large oriented single crystals of  $\beta$ -Li<sub>3</sub>TiF<sub>6</sub> and  $\beta$ -Li<sub>3</sub>VF<sub>6</sub>. These investigations are in progress and will be reported in the near future.

We thank *Prof. Dr. Arndt Simon* for his interest and support of this work. We are also indebted to *Dr. Reinhard K. Kremer* and *E. Brücher* for the susceptibility measurement and helpful discussions. The Stiftung Stipendienfonds des Verbands der Chemischen Industrie supported our research by a Stipend to *R.P.* 

### References

- [1] P. Ehrlich, G. Pictzka, Z. anorg. allg. Chem. 275 (1954) 121
- [2] S. Siegel, Acta Crystallogr. 9 (1856) 684
- [3] B. Babel, A. Tressaud, Crystal Chemistry of Fluorides in "Inorg. Chem. Solids" ed. P. Hagenmuller, Academic Press, INC, (1985) p 77
- [4] St. Becker, R. Hoppe, Z. anorg. allg. Chem. 579 (1989) 16
- [5] *R. Hoppe, St. Becker*, Z. anorg. allg. Chem. **568** (1989) 126
- [6] W. Massa, W. Rüdorff, Z. Naturforsch. 26b (1971) 1216
- [7] W. Massa, Z. Kristallogr. 153 (1980) 201
- [8] G. A. Sheldrick, SHELX-76, Program for Crystal Strcture Refinement, University of Göttingen, Germany (1976)
- [9] I. D. Brown, D. Altermatt, Acta Crystallogr. B41 (1985) 244
- [10] R. Hoppe, Angew. Chem. 92 (1980) 25; Angew. Chem., Int. Edn. Engl. 19 (1980) 10
- [11] R. Hoppe, J. Köhler, Z. Kristallogr. 183 (1988) 177
- [12] S. Geller, J. Chem. Phys. 33 (1960) 676
- [13] J. H. Burns, A. C. Tennissen, G. D. Brunton, Acta Crystallogr. B24 (1968) 225
- [14] S. Becker, B. G. Müller, Angew. Chem. 102 (1990) 426
- [15] R. Hoffmann, J. Chem. Phys. 39 (1963) 1397
- [16] J. H. Ammeter, H. B. Bürgi, J. C. Thibeault, R. Hoffmann, J. Amer. Chem. Soc. 100 (1978) 3686
- [17] M. H. Whangbo, R. Hoffmann, J. Amer. Chem. Soc. 100 (1978) 6093
- [18] R. Ramirez, M. C. Böhm, Int. J. Quantum Chem. 30 (1986) 391
- [19] R. H. Summerville, R. Hoffmann, J. Amer. Chem. Soc. 98 (1976) 7240
- [20] J. Köhler, PC-Version of the Program EHMACC (Extended-Hückel-Program, writen by M. H. Whangbo, R. Hoffmann, modified by M. Evain, J. Mitchel, Stuttgart, 1991
- [21] Parameters used in the EH calculations: Atomic orbitals energies: Hij [eV] (coefficients ζ1) for F: 2s -40.185 (2.425), 2p -18.5 (2.425); Ti: 4s -6.08 (1.500), 4p -3.85 (1.500), 3d -10.78 (4.55). Double ζ functions were used for Ti: d C<sub>1</sub> 0.4206, ζ<sub>2</sub> 1.40 and C<sub>2</sub> 0.7839
- [22] C. Mealli, D. Proserpio, J. Chem. Ed. 67 (1990) 333
- [23] R. Hoppe, Angew. Chem. 78 (1966) 52; Angew. Chem., Int. Edn. Engl. 5 (1966) 95
- [24] R. Hoppe, Adv. Fluorine Chem. 6 (1970) 387
- [25] M. Gerloch, J. Chem. Soc. 17 (1968) 2023
- [26] B. N. Figgis, Trans. Faraday Soc. 57 (1961) 198

#### Correspondence Address:

Dr. R. Pöttgen and Priv.-Doz. Dr. J. Köhler Max-Planck-Institut für Festkörperforschung Heisenbergstraße 1 D-70569, Stuttgart/Germany

Dr. A. K. Tyagi Applied Chemistry Division Bhabha Atomic Research Centre Trombay, Bombay (400 085), India