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The fluoroperovskite TlMnF₃


Dedicated to Professor Bernt Krebs on the Occasion of his 80th Birthday

Abstract: TlMnF₃ has been obtained from the reduction of Tl₃MnF₆ under liquid ammonia in which Mn(III) is obviously not redox-stable under the applied conditions. The crystal structure of TlMnF₃ has been determined on a single crystal using X-ray diffraction. The previous structure model was deduced from powder X-ray diffraction data only and therefore a much higher precision has been reached now. The compound crystallizes in the shape of colorless cubes with lattice parameters a = 4.2370(4) Å, V = 76.06(2) Å³ with Z = 1 at T = 140 K in the perovskite structure type (Pn3m, No. 221). At room temperature (T = 293 K), the lattice parameters of the slight pink, almost colorless bulk phase are a = 4.2535(2) Å, V = 76.953(4) Å³. As the displacement parameter of the Tl atom was observed being rather large in comparison, the CAIT technique was used to study the mobility of the Tl cations. Additionally, quantum chemical calculations were carried out to further investigate the behavior of the Tl atoms. We calculate that most of the Tl atoms vibrate already at 75 K. Magnetic measurements showed that TlMnF₃ is an antiferromagnet with T_N = 82 K and a Weiss temperature of −151.2(2) K.

Results and Discussion

We obtained TlMnF₃ from the reaction of Tl₃MnF₆ with liquid ammonia at −40 °C. Among powdery material, colorless-appearing crystals of TlMnF₃, suitable for single crystal X-ray diffraction, were obtained. The reaction proceeds likely according to the idealized equation 1.

\[ 6 \text{TlMnF}_6 + 8 \text{NH}_3 \rightarrow 6 \text{TlMnF}_3 + 12 \text{TiF} + 6 \text{NH}_4\text{F} + \text{N}_2 \]  

(1)

Obviously, the Mn(III) compound is not stable towards reduction by NH₃ under the selected conditions. We also synthesized TlMnF₃ by annealing TiF and MnF₂ in stoichiometric amounts in sealed platinum ampoules according to equation 2.

\[ \text{TiF} + \text{MnF}_2 \rightarrow \text{TlMnF}_3 \]  

(2)

The bulk phase looked slightly pink as is expected for Mn(II) compounds and was obtained phase pure as evidenced by powder X-ray diffraction (see Figure S1 for the LeBail fit). The bulk phase has the lattice parameters a = 4.2535(2) Å, V = 76.953(4) Å³, T = 293 K, which is in good agreement with the isotypic compounds AMnF₃ (A = K, NH₄, Rb, Cs).[1-3] As it is long known that TlMnF₃ crystallizes in the perovskite type structure, no detailed structure description will be given in the following. Figure 1 shows a section of the crystal structure of the compound and Tables 1 and 2 contain crystallographic details. Perovskites have been studied in detail also using purely geometric considerations and relations of atomic radii / lattice parameters have been set up.[4]
Using the Shannon radii for the atoms, a Goldschmidt tolerance factor of $t = 1$ is obtained for our TlMnF$_3$. It states that when $t$ is in the range of 0.89 to 1 the perovskite is cubic, and for $t = 1$ the cations are in contact with the anions. When 1.285 Å is used for the radius of the F atom ($r_f$) for C.N. = 2 (which is known to reproduce M–F distances best), and $a = 4.252$ Å (powder, 293 K), then $r_{Mn} = 0.842$ Å and $r_{Tl} = 1.723$ Å are obtained which are very close to the Shannon radii ($r_{Mn} = 0.83$ Å and $r_{Tl} = 1.70$ Å). It is interesting to note that the displacement parameter of the Tl atom is rather large in comparison to the lighter Mn atom (Figure 1). We conducted refinements (also on crystals of different batches) in space groups of lower symmetry and/or using twinning or disorder models, however none of these yielded better results and no deviation from the cubic symmetry could ever be observed. We conducted therefore determinations of the single crystal structure at different temperatures to obtain the temperature-dependent $U_{iso}$ values of the Tl atoms. Figure 2 shows a plot of the $U_{iso}$ values versus the measurement temperature. The linear fits to the data show that the $U_{iso}$ values of the heavy atoms become essentially 0 at 0 K. That indicates that the displacement parameters are mainly influenced by thermal effects. Therefore, the larger displacement parameter of the heavier Tl atom is likely due to the larger space available in the cubeoctahedral coordination polyhedron in comparison to the one of the lighter Mn atom with its octahedral coordination. We also investigated the structure of TlMnF$_3$ using quantum chemical methods to check if the cubic perovskite structure is indeed a true local minimum (DFT-PBE0/SVP level of theory). Since Mn(II) is a magnetic ion, we first investigated the magnetic ground state of the system. The antiferromagnetic ground state proved to be energetically favorable over a ferromagnetic configuration by 2.3 kJ/mol. The optimized lattice parameter $a$ is in excellent agreement with the X-ray structure, being only 0.4 % larger than the experimental structure. After the geometry optimization, we ran a harmonic frequency calculation to investigate the nature of the stationary point at the potential energy surface. According to the frequency analysis, all frequencies in the system are real, suggesting that the proposed structure is a true local minimum. The calculated harmonic frequencies vary between 52 and 495 cm$^{-1}$, the lowest-energy frequencies (52 and 68 cm$^{-1}$) correspond to the movement of the Tl atoms. As 52 cm$^{-1}$ convert into 75 K at which most of the Tl atoms vibrate, the rather large displacement parameter of the Tl atom is likely due to the thermal motion of the Tl atoms. These investigations raise the question whether further evidence for any relevant mobility of the Tl cation can be found. To this end we have employed the charge attachment induced transport (CAIT) technique combined with subsequent time-of-flight secondary ion mass spectrometry (ToF-SIMS), which is capable of unraveling the identity of mobile charge carriers in a solid sample. Here, attachment of low energy Rb$^+$ ions to the surface of a TlMnF$_3$ pellet induces transport of any mobile charge carrier inside the sample. As further outlined in the supporting information these experiments demonstrate that the Tl$^+$ ions exhibit significant mobility. This conclusion is based on the observation that Tl$^+$ is effectively replaced by the Rb$^+$ ions in the region near to the surface of the sample. This replacement is indeed plausible since the radii of the two cations are very similar. The mobility of the Mn$^{2+}$ and F$^-$ ions is much smaller than that of the Rb$^+$ ions. Therefore, the large displacement parameter is most likely caused by the cubeoctahedral space providing for the intrinsic mobility of the Tl$^+$ ions. Finally the electrical conductivity of the TlMnF$_3$ sample has been measured as $\sigma_{DC} = 8.1 \times 10^{-11}$ S/cm at 303 K, the activation energy is $E_{act} = (0.19 \pm 0.02)$ eV.

### Table 1. Wyckoff positions, site symmetries, fractional atomic coordinates and isotropic displacement parameters of TlMnF$_3$ at 140 K.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>Site symmetry</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso}$ / Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>1a</td>
<td>m$\bar{3}$m</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.00313(18)</td>
</tr>
<tr>
<td>Tl</td>
<td>1b</td>
<td>m$\bar{3}$m</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>0.00787(14)</td>
</tr>
<tr>
<td>F</td>
<td>3d</td>
<td>4/mmm</td>
<td>0</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>0.0088(6)</td>
</tr>
</tbody>
</table>

Figure 1. Isotropic displacement parameters of the atoms of TlMnF$_3$ plotted versus the temperature.

Figure 2. A section of the crystal structure of TlMnF$_3$ viewed along the c-axis. Displacement parameters are shown at 70 % probability level at 140 K. Numbers indicate the height of the atoms in the unit cell.

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Table 2. Crystallographic details of the structure determination.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sum formula</td>
<td>TlMnF₃</td>
</tr>
<tr>
<td>Formula weight /g mol⁻¹</td>
<td>316.31</td>
</tr>
<tr>
<td>Crystal dimensions /mm³</td>
<td>0.1·0.1·0.1</td>
</tr>
<tr>
<td>Crystal description</td>
<td>Colorless cuboid</td>
</tr>
<tr>
<td>Crystal system</td>
<td>cubic</td>
</tr>
<tr>
<td>Space group (no.)</td>
<td>Pm̅3m, (No. 221)</td>
</tr>
<tr>
<td>a / Å</td>
<td>4.2370(4)</td>
</tr>
<tr>
<td>V / Å³</td>
<td>76.06(2)</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
</tr>
<tr>
<td>ρcalc. / g cm⁻³</td>
<td>6.905</td>
</tr>
<tr>
<td>ρtrue / g cm⁻³ (T = 298 K)</td>
<td>6.80(1)</td>
</tr>
<tr>
<td>μ / mm⁻¹</td>
<td>56.89</td>
</tr>
<tr>
<td>F(000)</td>
<td>133</td>
</tr>
<tr>
<td>Temperature /K</td>
<td>140(2)</td>
</tr>
<tr>
<td>Wavelength /Å</td>
<td>0.71073 (MoKα)</td>
</tr>
<tr>
<td>Θ range /°</td>
<td>4.81 – 41.33</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-6 ≥ h ≥ 7, -7 ≥ k ≥ 6, -7 ≥ l ≥ 7</td>
</tr>
</tbody>
</table>

Magnetic measurements show the compound to be an antiferromagnet with $T_N = 82$ K, a Weiss temperature $θ$ of $-151.2(2)$ K and a $n_{eff}$ of 6.271(2) Bohr magnetons (Figure 3). The theoretical spin-only value for Mn(II) is reported to be 5.92 Bohr magnetons, and observations have been made in the range from 5.7 to 6.1 Bohr magnetons. The bump in the magnetization curve at circa 50 K is due to an unknown impurity as measurements on several different samples showed an increase or decrease in its magnitude. Therefore the deviation of the $n_{eff}$ observed by us is likely due to this impurity.

Conclusions

Single crystals of TlMnF₃, which crystallizes in the perovskite structure type, were either obtained by reaction of Tl₃MnF₆ in liquid ammonia at $-40$ °C and subsequent warming to room temperature driving off the NH₃, or by melting TIF with MnF₂ in Pt ampoules at 830 °C. The compound shows antiferromagnetic behavior with $T_N = 82$ K and a Weiss temperature $θ$ of $-151.2(2)$ K. As the displacement parameter of the Tl atom was found to be rather large, temperature dependent determinations of the $U_{iso}$ values, quantum chemical calculations, as well as the CAIT technique were used to study the vibrations and thermal mobility of the Tl cations. The electrical conductivity of the TlMnF₃ sample has been measured as $σ_{DC} = 8.1 \times 10^{-11}$ S/cm at 303 K.

Experimental Section

The lilac moisture sensitive compound Tl₃MnF₆, thallium hexafluoridomanganate(III), was received as a donation from the late Prof. Hoppe (Justus-Liebig-Universität Giessen, Germany). Hoppe and coworkers obtained it by the reaction of TIF and MnF₂ in sealed Au ampoules and annealing not more than six days at temperatures not higher than 480 °C.[19] 134 mg (0.17 mmol) of Tl₃MnF₆ was reacted with approximately 10 mL of anhydrous liquid ammonia at $-40$ °C. The reaction vessel was stored for five months at $-40$ °C to allow for crystallization. The violet color vanished during this time and the insoluble solid became a brownish-yellow. Among the brown-yellow solid, colorless single crystals
were observed under the microscope of which a suitable specimen was selected for single crystal X-ray diffraction at 140 K. X-ray structure analysis on a single crystal of the compound was carried out by using an Stoe IPDS 2 diffractometer with monochromated molybdenum radiation (MoKα, λ = 0.71073 Å) and an image plate type detector. Crystals were mounted using the MiTeGen MicroLoop system. The structure was solved using Direct Methods (SHELXT-14) and refined against \( F^2 \) (SHELXL-18). The atoms were located by Difference Fourier synthesis and refined anisotropically in case of F, and isotropic in case of Mn and Ti (due to the site symmetry). The residual electron density is located close to the Ti atom.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49 7247 808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition numbers CSD-434329.

TI\(\text{MnF}_3\) was also obtained by direct reaction of TIF with Mn\(\text{F}_2\) in sealed platinum ampoules. A typical synthesis used 353.15 mg (1.581 mmol) of TIF and 146.92 mg (1.851 mmol) of Mn\(\text{F}_2\) in order to obtain 500 mg of TI\(\text{MnF}_3\). The reaction mixture was warmed with 10 °C/min from room temperature to 330 °C, kept for 5 h, then warmed with 1 °C/min to 830 °C, annealed for 2 h, and then cooled slowly (0.05 °C/min) to 770 °C and then with a rate of 5 °C/min to room temperature. The compound was obtained phase pure as evidenced by powder X-ray diffraction.

DC-magnetic data were collected with the aid of the VMS option of a physical property measurement system (PPMS) of LOT-Quantum Design. Temperature dependent magnetic data were recorded in the range from 1.8 K to 350 K with an applied field of 0.1 T. The collected data were corrected with respect to the diamagnetic moment of the sample holder, as well as to the diamagnetic contribution of the sample derived from Pascal constants taking into account the composition of the compound, the result being the net paramagnetic data.

For the transport experiment a beam of Rb\(^+\) ions has been aimed at the front side of a Ti\(\text{MnF}_3\) pellet under high vacuum conditions (10\(^{-6}\) mbar). The sample has been in contact with a metal electrode (Cu) at the backside which in turn was connected to a transimpedance amplifier. The Rb\(^+\) ion beam was operated at 30 Volt. Attachment of Rb ions to the surface of the sample induces the buildup of an electrical surface potential and consequently a gradient of the electrochemical potentials. The effective voltage drop across the sample is maintained small in order to avoid electrochemical decomposition of the sample. Mobile cations in the sample will move towards the backside electrode. This requires pulling the ions into the sample, which generates a concentration depletion profile. Ultimately, a long-term Rb\(^+\) ion attachment has been performed for a total of approximately 300 hours during which a total charge of 35 mC has been transported through the sample. The sample temperature has been set to 348 K.

Directly after the transport experiment the sample has been transferred to a time-of-flight secondary ion mass spectrometry (ToF-SIMS) machine (ToF-SIMS 5, IONTOF GmbH, Münster, Germany) for concentration depth profiling. A bismuth liquid metal ion gun (LMIG) and an oxygen sputter gun are operated in the non-interlaced mode. The ToF-MS employed exhibits a mass resolution \( m/\Delta m \) of approximately 6000. The following settings were used for the ToF-SIMS depth profiling. The LMIG was operated with Bi\(^+\) ions at 25 keV, whereas the DSC sputter gun was operated at 3 keV acceleration voltage. The analysis area was approximately 100 µm x 100 µm, while the sputter area was 300 µm x 300 µm. An electron flood gun has been used to avoid charging up of the sample during the depth profiling. The detector was operated in the positive ion mode.

The DC conductivity and the activation energy for charge carrier transport have been measured by bringing the sample into contact with two copper electrodes and measuring conventional current–voltage data as function of the temperature between 303 K and 343 K.

Quantum chemical calculations for solid-state Tl\(\text{MnF}_3\) were carried out using the PBE0 hybrid density-functional (DFT) method.\(^{[23,24]}\) A split-valence + polarization level basis (SVP) was applied for all atoms. The basis sets were derived from the def2-SVP basis set (details and full basis set listing in Supporting Information).\(^{[25]}\) The basis set for fluorine was taken from a previous study. All calculations were carried out using the CRYSTAL14 program package with spin-unrestricted formalism.\(^{[26]}\) For a ferromagnetic spin configuration, the primitive cell of Tl\(\text{MnF}_3\) was applied. For antiferromagnetic configuration, a 2×2×2 supercell was constructed and the resulting calculations could be carried out in the \(\text{Fm\overline{3}m}\) supergroup of the original \(\text{Fm\overline{3}m}\) space group. The used input structures are given as Supporting Information. The reciprocal space was sampled using a 8×8×8 and 6×6×6 Monkhorst-Pack-type \( k \)-point grids for the ferromagnetic and antiferromagnetic structures, respectively.\(^{[27]}\) For the evaluation of the Coulomb and exchange integrals (TOLINTEG), tight tolerance factors of 8, 8, 8, 8, and 16 were used. Both the atomic positions and lattice constants were fully optimized within the constraints imposed by the space group symmetry. Default optimization convergence thresholds and an extra-large DFT integration grid (XLGRID) were applied in all calculations. The harmonic vibrational frequencies were obtained through the use of the computational scheme implemented in CRYSTAL.\(^{[28,29]}\)

**Acknowledgements**

F.K. thanks the DFG for funding. Sarah Karmel for the initial sample preparation from liquid \(\text{NH}_3\) and Solvay for the generous donation of \(\text{F}_2\). Computational resources were provided by CSC, the Finnish IT Center for Science (A.J.K.).

**Keywords:** thallium • manganese • fluoride • perovskite structure type • magnetism


\(^{[6]}\) M. P. Petrov, G. A. Smolenskii, Fizika Tverdogo Tela (Sankt-Petersburg) 1965, 7, 2156–2161.


The single crystal structure of TlMnF$_3$ has been determined. The compound is an antiferromagnet and shows significant Tl$^+$ mobility.
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