207Pb and 205Tl NMR on Perovskite Type Crystals APbX₃ (A = Cs, Tl, X = Br, I)

Surendra Sharma, Norbert Weiden, and Alarich Weiss

Institut für Physikalische Chemie, Physikalische Chemie III, Technische Hochschule Darmstadt, West Germany

Z. Naturforsch. 42a, 1313–1320 (1987); received August 24, 1987

Dedicated to Prof. Dr. K. G. Weil to the Occasion of his 60th Birthday

By 207Pb and 205Pb NMR the chemical shift in polycrystalline samples of binary halides AX, BX₃ and ternary halides ABX₃ (A = Cs, Tl; B = Pb; X = Br, I) was studied at room temperature. The chemical shift tensors δ(205Tl) and δ(207Pb) were determined in magnitude and orientation on single crystals of the orthorhombic TlPbI₃. The components of the δ(205Tl) tensor are: δ(205Tl) || a = 611 ppm; δ(205Tl) || b = 680 ppm; δ(205Tl) || c = 1529 ppm; δiso(205Tl) = 873.3 ppm (with respect to 3.4 molal aqueous solution of Tl(OAc)₃). The chemical shift tensor of 207Pb in TlPbI₃ shows two orientations. One of them is: δ(207Pb) = 3760 ppm, inclined 30° from b towards c, δ(207Pb) || a = 3485 ppm, δ(207Pb) || b = 2639 ppm inclined 120° from b towards c. δiso(207Pb) = 3295 ppm (with respect to saturated aqueous solution of Pb(NO₃)₂). The results are discussed with respect to the crystal structure and a model to explain orientation and anisotropy of the tensors δ(205Tl) and δ(207Pb) in TlPbI₃ is proposed.

In the system CsPbBr₃...I, δ(207Pb) was studied on polycrystalline samples. The chemical shift increases with increasing x and negative excess shift is observed.

Introduction

A very simple arrangement of the ions (atoms) in a solid compound ABX₃ is the cubic perovskite type structure with one formula unit in the elementary cell, with the space group O₃m - Pm3m, and the atoms in 0, 0, 0 (A), 0, 1, 0, 1/2, 1/2, 1/2 (B) and 1/2, 0, 1/2, 1/2, 0, 1/2, 0, 1/2, 1/2, 0, 1/2, 0, 0, 1/2, 0, 1/2, X). In case of highly polarizable atoms (ions) A and X and strongly polarizing atoms (ions) B changes of temperature and/or pressure and thereby the decrease in interatomic distances leads to phase transitions. The classical example is BaTiO₃ in which the cubic perovskite structure changes into a polar one showing ferroelectricity and other properties connected with its strong uniaxial polarization.

Considering such physical properties, an interesting group of compounds ABX₃ are ternary halides with A = alkali metal atom, B = element of the group IV (Ge, Sn, Pb), and X = F, Cl, Br, I. The polarizabilities of A and X, respectively, increase with increasing atomic number whereas the B elements have increasing polarizing power with decreasing atomic number. Wide variations of crystal structures, phase transitions, and physical properties occur by using the wide range of chemical combinations within this group of ABX₃ compounds. Quite a large number of investigations has been devoted to the halides ABX₃ in recent years.

A well studied compound out of the group under discussion is CsPbCl₃. The phase transitions have been investigated by X-ray and neutron diffraction [1–7], Raman scattering [1,8], ultrasorons [6,9,10], nuclear magnetic resonance, NMR [11], and nuclear quadrupole resonance, NQR [12–14]. Measurements of thermal expansion, birefringence, dielectric properties, and the specific heat have been reported [7,10,15–17] as well as studies of the influence of hydrostatic pressure on the phase transitions [18]. Combining EPR on Gd³⁺ doped CsPbCl₃ crystals and measurements of dielectric properties, Cohen et al. [19] observed six different phases in the temperature range 170 ≤ T/K ≤ 320. A pyroelectric phase was observed thereby in the range 175 ≤ T/K ≤ 193.

The transition from the cubic high temperature phase to the tetragonal phase II is – as in the system CsPbBr₃ [20,21], too – of first order and of tilting type. It is connected with a soft mode condensation [5]. Following transitions to low temperature phases result in orthorhombic unit cells (CsPbCl₃, CsPbBr₃ [5,21]), and monoclinic phases have been observed, too (CsSnCl₃ [22]).
Several studies have been reported for the compounds CsSnX₃, with X = Cl, Br, I. Scaife et al. [23] studied these systems by X-ray diffraction and by NQR and Barrett [24] conducted Sn-Mössbauer spectroscopy on these ternary Sn(II) halides. Investigations on mixed crystals CsSnBr₃₋ₓYₓ, Y = Cl, I, have been included in the work of these authors.

The high temperature perovskite type phase of CsGeCl₃ changes to a rhombohedral low temperature phase (space group R3, Z = 1, T_c = 155°C), and this phase exhibits ferroelectricity with a dielectric constant comparable to that of BaTiO₃ [25]. Here the stronger polarizing power of Ge²⁺ compared to Sn²⁺, respectively. The rubidium compound is a semiconductor whereas CsGeI₃ shows metallic conductivity [27].

Strong anharmonic lattice vibrations of the X-ions have been observed for CsPbX₃ (X = Cl, Br) [2-4], and in turn Mizusaki et al. [28] found halogen ion conductivity in these compounds; the conductivity is comparable to that of PbCl₂ and PbBr₂, respectively. The rubidium compound is a semiconductor whereas CsGeI₃ shows metallic conductivity [27].

In the following we report 207Pb and 205Tl NMR studies on AX, PbX₂, and APbX₃, A = Cs, Tl; X = Br, I and on mixed crystals in these ternary halides.

Experimental

Preparation, Single Crystal Growth

All compounds studied have been synthesized by melting together the stoichiometric amounts of the reagent grade constituent chemicals. TIBr, PbBr₂, and PbI₂, all 99%, were obtained from E. Merck, Darmstadt. CsBr (> 99%) and CsI (> 99.5%) were purchased from Fluka, Basel.

The constituents were dried and sealed in supremax glass ampoules under vaccum. They were heated to 50 K above the melting point of the respective compound ABX₃. The melt was kept at this temperature for about seven hours and shaken well at intervals to ensure homogeneity. Polycrystalline samples and samples of mixed crystal systems were made following this procedure. TIPbI₃ was purified ten times by zone melting (8 mm/h). The purified material was transparent and red in colour. The middle part of the zone refined regulus thus obtained was used for growing single crystals. Since CsPbBr₃ reacts slightly with glass [36] only four zone refining cycles were done for this material.

Large crystals of TIPbI₃ and CsPbBr₃ were grown from the zone refined material by Bridgeman technique. A temperature gradient of ~30 K/cm at the connecting position of the upper (T > T_mel) and the lower (T < T_mel) furnace and a lowering rate of 1 mm/h for the sample tube was found satisfactory for the growth of both materials. The crystal structure of TIPbI₃ has been determined by Stoeger [37] (orthorhombic, space group D₁₇h-Cmcm; Z = 4).
crystals cleave easily along the plane (001) [37]. A crystal of \((10 \times 10 \times 10) \text{mm}^3\) in size was cut and mounted on a one circle goniometer in the magnet with the help of an optical goniometer in such a way that it could be rotated around the three orthogonal axes \(a, b,\) and \(c\), respectively, depending on the mounting.

\(207\text{Pb} \text{ and } 205\text{Tl NMR Measurements}\)

The chemical shift \(\delta\) of the \(205\text{Tl}\) and \(207\text{Pb}\) NMR signal has been measured in a magnetic field of 4.7 Tesla using a pulse spectrometer. The free induction decay (FID) was accumulated and transformed into the frequency domain by fast Fourier transform (FFT).

All experiments were carried out at room temperature with a spectrometer frequency of 41.890 MHz and 115.500 MHz for the \(207\text{Pb}\) and \(205\text{Tl}\) nuclei, respectively. Up to 5000 acquisitions were necessary to obtain the \(207\text{Pb}\) NMR signals with a signal to noise ratio \((S/N)\) of about 20; fewer acquisitions are necessary to have a \(205\text{Tl}\) NMR signal of \(S/N = 20\).

The chemical shift \(\delta\) of the NMR signal of a particular nucleus in a certain sample is defined with respect to the NMR frequency of the nucleus in a reference compound \(v_{\text{ref}}\) in identical external fields \(B_0\) by

\[
\delta = (v - v_{\text{ref}})/v_{\text{ref}},
\]

with \(v = \) resonance frequency of the nucleus in the sample considered. A 3.4 molar aqueous solution of Tl(I)-acetate, \(\text{TlOOCCH}_3\), has been used as reference sample (external standard) for \(205\text{Tl}\) and a saturated (295 K) aqueous solution of lead nitrate, \(\text{Pb(NO}_3\text{)}_2\), for \(207\text{Pb}\). Absolute NMR frequencies of 115.4655 MHz \((205\text{Tl})\) and 41.7418 MHz \((207\text{Pb})\) have been determined for the reference samples. An extrapolation to infinite dilution gives \(\delta = 192 \text{ ppm}\) for \(205\text{Tl}\) and \(\delta = -70 \text{ ppm}\) for \(207\text{Pb}\) of our references with respect to those of ideal sample signals at infinite dilution [38, 39] and own measurements.

Results

In Fig. 1 a typical NMR signal of \(205\text{Tl}\) in polycrystalline \(\text{TIPbBr}_3\) is shown. The line is broad (~ 450 ppm line width), preventing a determination of the anisotropy of the chemical shift tensor in polycrystalline material. Figure 2 summarizes all chemical shift measurements done in this work on polycrystalline compounds. The values for the isotropic chemical shift \(\delta_{\text{iso}}\) of \(205\text{Tl}\) and \(207\text{Pb}\) found by single crystal measurements on \(\text{TIPbI}_3\) are also given. The isotropic shift is defined by

\[
\delta_{\text{iso}} = \frac{1}{3}(\delta_x + \delta_y + \delta_z).
\]

The deviation of \(\delta_{\text{iso}}\) from the \(\delta\)-value of the respective polycrystalline sample causes the high anisotropy of

---

Fig. 1. NMR signal of \(205\text{Tl}\) in polycrystalline \(\text{TIPbBr}_3\). The chemical shift against \(v_{\text{ref}}(205\text{Tl}) = 115.4655 \text{ MHz}\) is 645 ppm; the line-width is about 450 ppm. \(T = 295 \text{ K}\).

Fig. 2. Chemical shift of \(205\text{Tl}-\text{NMR}\) (a) and \(207\text{Pb}-\text{NMR}\) (o) in polycrystalline samples vs. mole fraction of right hand compound. The values for the isotropic chemical shifts \(\delta_{\text{iso}}\) in \(\text{TIPbI}_3\) calculated from single crystal measurements are also shown. External standards were: 3.4 molar aqueous solution of \(\text{TIOOCCH}_3\), \(v_{\text{ref}}(205\text{Tl}) = 115.4655 \text{ MHz}\) and saturated solution of \(\text{Pb(NO}_3\text{)}_2\), \(v_{\text{ref}}(207\text{Pb}) = 41.7418 \text{ MHz}\). \(T = 295 \text{ K}\).
the chemical shift tensor. Due to the line width the anisotropy could not be measured on polycrystalline samples at room temperature, and the center of the line is not identical with $\delta_{\text{iso}}$.

The line width of the NMR signals in single crystals is 20–30% lower than that in polycrystalline samples. The angular dependence of the thallium chemical shift, $\delta^{\text{205Tl}}(\text{TlPbI}_3)$, in single crystals of TlPbI$_3$ was measured using the crystal axes $a$, $b$, and $c$, respectively, as rotation axes $\perp B_0$.

The results are shown in Figs. 3 and 4. It is seen that the rotation around $a$ exhibits strong angular dependence of $\delta^{\text{205Tl}}$ and a high anisotropy of the chemical shift tensor is expected. The rotation around $b$, the results of which are shown in Fig. 4, supports this conclusion.

The variation of the $^{207}\text{Pb}$ NMR chemical shift in TlPbI$_3$ with the rotation angle $x$ is shown for the rotation around the axes $b$ and $c$ in Figure 5. The dependence $\delta^{\text{207Pb}}(\text{Pb}) = f(x)$ with $c \perp B_0$ is very small while the rotation around the axis $a$ (Fig. 6) clearly points out that (a) there are two tensors for the lead NMR shift, with the tensor axes inclined $120^\circ / 60^\circ$ to each other and (b) the anisotropy of the chemical shift is large for $^{207}\text{Pb}$, too.

### Discussion

In Table 1 we have summarized the information about the crystal structures of ternary halides $\text{ABX}_3$ studied here. CsPbBr$_3$ and CsPbI$_3$ are isomorphous at room temperature.
Table 1. Crystal structures of ternary halides \( \text{APbX}_3 \) with \( A = \text{Cs, TI} \) and \( X = \text{Br, I} \).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature range/K</th>
<th>Space group Z</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CsPbBr}_3 )</td>
<td>403 and up</td>
<td>( \text{O}_h^1 - \text{Pm}3\text{m} ) 1</td>
<td>[21]</td>
</tr>
<tr>
<td>( \text{CsPbI}_3 )</td>
<td>583–749</td>
<td>( \text{C}_2\text{h}^1 - \text{P}2_1/\text{m} ) 1</td>
<td>[44]</td>
</tr>
<tr>
<td>( \text{TlPbI}_3 )</td>
<td>295–619</td>
<td>( \text{D}_{2\text{h}}^5 - \text{Cmc} \text{m} ) 4</td>
<td>[37]</td>
</tr>
<tr>
<td>( \text{TlPbBr}_3 )</td>
<td>not known</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 6. Angular dependence of the lead chemical shift \( \delta(207\text{Pb}) \) in \( \text{TlPbI}_3 \). Rotation around \( a \)-axis. \( T = 295 \text{ K} \).

The chemical shift measurements on polycrystalline samples \( \text{TlX, PbX}_2 \), and \( \text{ABX}_3 \) (\( A = \text{Cs, TI} \); \( X = \text{Br, I} \)) show for the \( ^{205}\text{TI} \) as well as for \( ^{207}\text{Pb} \) an increase of the shift when bromine is replaced by iodine (see Figure 2). This is the general tendency for the combinations \( \text{TIBr} \rightarrow \text{TII} \), \( \text{PbBr}_2 \rightarrow \text{Pbl}_2 \), \( \text{TlPbBr}_3 \rightarrow \text{TlPbI}_3 \), and \( \text{CsPbBr}_3 \rightarrow \text{CsPbI}_3 \). The change of \( \delta(207\text{Pb}) \) is stronger than that for \( \delta(205\text{TI}) \) whereas in the case of the pair \( \text{TlPbBr}_3 \rightarrow \text{TlPbI}_3 \) it is quite small. The data extracted from measurements on polycrystalline samples are listed in Table 2.

Hafner and Nachtrieb [38, 40] have made an extensive study of \( \delta(\text{TI}) \) for the halides of \( \text{Tl(I)} \); \( \text{TIF, TICI, TlBr, and TII} \). It should be noted that the value for \( \delta(205\text{TI}) \) in \( \text{TlBr} \) agrees well with that of Hafner and Nachtrieb [38] if \( \delta(205\text{TI}) \) is calculated with respect to a common standard: Aqueous solution of \( \text{Tl}^{\circ} \) ions at infinite dilution. In case of \( \text{TII} \) there is no agreement between the data of Hafner and Nachtrieb [38], Hinton and Metz [35], and ours. The value given by Hinton and Metz measured at elevated temperatures can be taken for comparison, too, since \( \delta(205\text{TI}) \) is almost independent of temperature in the cubic phase of \( \text{TII} \) [38]. The shifts calculated with respect to a reference sample, at infinite dilution and at room temperature, are: \( \delta(205\text{TI}) \) in \( \text{TlBr} \): 815 ppm [38], 837 ppm (this work), \( \delta(205\text{TI}) \) in \( \text{TII} \): 1770 ppm [38]; 1180 ppm (at 401 K) [35]; 1582 ppm (this work). For solid solutions \( \text{TICl}_x\text{Br}_{1-x} \), Hafner [41] found an almost linear dependence \( \delta(\text{TI}) = f(x) \). The increase of \( \delta(\text{TI}) \) by the exchange \( \text{Br} \rightarrow \text{I} \) was discussed by these authors in the framework of Ramsey’s theory of chemical shift [42] and a simplified Heitler-London model used by Yosida and Moriya [43]. According to them an increase of covalency by the exchange \( \text{Br} \rightarrow \text{I} \) leads to an increase in \( \delta(\text{TI}) \). For the mixed crystal system \( \text{(CsPbBr}_3\text{)}_{1-x}\text{(CsPbI}_3\text{)}_x \), the present results show clearly that the exchange \( \text{Br} \rightarrow \text{I} \) raises \( \delta(207\text{Pb}) \) in accordance with the observation for \( \text{PbBr}_2 \rightarrow \text{Pbl}_2 \), for which no chemical shift data could be found in the literature. However, in contrast to the system \( \text{TICI}_x\text{Br}_{1-x} \), we do not find a linear dependence \( \delta(207\text{Pb}) = f(x) \) but a negative excess chemical shift which cannot be explained at present. The small increase in \( \delta(205\text{TI}) \) within the system \( \text{TlPbBr}_3 \rightarrow \text{TlPbI}_3 \) is in contrast to

Table 2. Resonance frequencies \( \nu \) and chemical shifts \( \delta \) in polycrystalline samples of \( \text{TlX, PbX}_2 \), and \( \text{ABX}_3 \) (\( A = \text{Cs, TI} \); \( X = \text{Br, I} \)) at 295 K. \( \delta \) is given with respect to the external standards: 3.4 molar aqueous solution of \( \text{TIO}_2\text{CCH}_3 \) and saturated aqueous solution of \( \text{Pb(NO}_3\text{)}_2 \). The values of \( \delta \) with respect to infinite dilution of the standard can be found by adding 192 ppm to \( \delta(205\text{TI}) \) and subtracting 70 ppm from \( \delta(207\text{Pb}) \).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nucleus</th>
<th>( \nu/\text{MHz} )</th>
<th>( \delta/\text{ppm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{TlPbI}_3 )</td>
<td>( ^{205}\text{TI} )</td>
<td>115.544</td>
<td>680</td>
</tr>
<tr>
<td>( \text{TlPbBr}_3 )</td>
<td>( ^{205}\text{TI} )</td>
<td>115.540</td>
<td>645</td>
</tr>
<tr>
<td>( \text{TII} )</td>
<td>( ^{205}\text{TI} )</td>
<td>115.626</td>
<td>1390</td>
</tr>
<tr>
<td>( \text{TlBr} )</td>
<td>( ^{205}\text{TI} )</td>
<td>115.540</td>
<td>645</td>
</tr>
<tr>
<td>( \text{TlPbI}_3 )</td>
<td>( ^{207}\text{Pb} )</td>
<td>41.893</td>
<td>3622</td>
</tr>
<tr>
<td>( \text{CsPbI}_3 )</td>
<td>( ^{207}\text{Pb} )</td>
<td>41.918</td>
<td>4221</td>
</tr>
<tr>
<td>( \text{TlPbBr}_3 )</td>
<td>( ^{207}\text{Pb} )</td>
<td>41.820</td>
<td>1873</td>
</tr>
<tr>
<td>( \text{CsPbBr}_3 )</td>
<td>( ^{207}\text{Pb} )</td>
<td>41.878</td>
<td>3263</td>
</tr>
<tr>
<td>( \text{CsPbBrI}_3 )</td>
<td>( ^{207}\text{Pb} )</td>
<td>41.879</td>
<td>3287</td>
</tr>
<tr>
<td>( \text{CsPbBrI}_3 )</td>
<td>( ^{207}\text{Pb} )</td>
<td>41.890</td>
<td>3550</td>
</tr>
<tr>
<td>( \text{PbBr}_2 )</td>
<td>( ^{207}\text{Pb} )</td>
<td>41.829</td>
<td>2089</td>
</tr>
<tr>
<td>( \text{Pbl}_2 )</td>
<td>( ^{207}\text{Pb} )</td>
<td>41.866</td>
<td>2975</td>
</tr>
</tbody>
</table>
the strong one for the pair TIBr \( \rightarrow \) TIL. This should be compared with the \( \delta^{(207\text{Pb})} \) in the systems TIPbBr\(_{3} \rightarrow \) TIPbI\(_{3} \) and PbBr\(_{2} \rightarrow \) PbI\(_{2} \), respectively. In both cases the increase of the shift is fairly strong. We may argue that an exchange Br \( \rightarrow \) I has a strong influence on the atoms in the first coordination shell of the X-atoms but not so much in the second one. From the large change of \( \delta^{(207\text{Pb})} \) by going from TIPbBr\(_{3} \) to CsPbBr\(_{3} \), it is seen that a possible change of crystal structure has to be taken into account.

CsPbBr\(_{3} \) crystallizes orthorhombic while TIPbBr\(_{3} \) is not isomorphous as preliminary investigations have shown (see Table 1).

A further discussion concerning the influence of the exchange A \( \rightarrow \) A', B \( \rightarrow \) B', X \( \rightarrow \) X' on the chemical shift of NMR in ternary halides is not meaningful at present, if the data are based on measurements with polycrystalline samples. Broad lines (see Fig. 1) prohibit the determination of the anisotropy of the chemical shift tensor, and even in the case of recognizable anisotropy the direction of the principal axes of the chemical shift tensor are not obtained. A detailed discussion of correlations between chemical shift, coordination spheres, and interatomic distances is thus not possible.

**The Chemical Shift Tensors \( \delta^{(205\text{TI})} \) and \( \delta^{(207\text{Pb})} \) in TIPbI\(_{3} \)**

In Figs. 3–6 the results of the single crystal measurements, \( \delta^{(205\text{TI})} \) and \( \delta^{(207\text{Pb})} \) in TIPbI\(_{3} \) are shown. In Table 3 the principal axes of the chemical shift tensors in magnitude and orientation are listed. Figure 7 shows the projection of the unit cell along the axis [100]. In the space group \( D_{2h}^{17} = \text{Cmcm} \) the TI-atoms are located at the point position 4c with symmetry mm. Only one pattern \( \delta\) (TI) \( = f(x) \) is therefore expected, independent of the rotation axis (a, b, or c). The principal axes of the \( \delta\) (TI) tensor must be parallel to the crystal axes by symmetry conditions, too. The values for \( \delta_{x} \), \( \delta_{y} \), and \( \delta_{z} \) are given in Table 3. They have been calculated according to the definition

\[
|\delta_{x} - \delta_{\text{iso}}| \geq |\delta_{x} - \delta_{\text{iso}}| \geq |\delta_{y} - \delta_{\text{iso}}|. \tag{3}
\]

The \( \delta\) (TI)-tensor is almost rotational symmetric, \( \delta_{y} - \delta_{x} = 69 \) ppm, while the tensor is strongly stretched in the z-direction, \( \delta_{z} - \delta_{x} = 718 \) ppm.

In Fig. 8 the orientation of the principal axes of the \( \delta^{(205\text{TI})} \) tensor with respect to the first coordination sphere of TI in TIPbI\(_{3} \) are drawn. (Figure 8 should be compared with Figure 7.) One recognizes that the two axes with the nearly equal and small values of \( \delta^{(205\text{TI})} \), \( \delta_{x}^{(205\text{TI})} \), and \( \delta_{y}^{(205\text{TI})} \) are located in a plane formed by the TI atom and two iodine atoms I(2). \( \delta_{x}^{(205\text{TI})} \) is parallel to the line I(2)-I(2) and \( \delta_{y}^{(205\text{TI})} \) bisects the angle \( \angle \) (I(2)-TI-I(2)). In Table 4 the next nearest neighbour interatomic distances are listed. The distances TI-I(2) are 346.7 pm which are the shortest TI-I distances in TIPbI\(_{3} \). The chemical shift of the \( ^{205}\text{TI} \) NMR to the lowest frequencies (at \( B_{0} = \) constant) is therefore strongly correlated to the shortest distance TI-I which, most probably, involves the strongest interaction between TI and I. A similar relation was obtained between the chemical shift of

<table>
<thead>
<tr>
<th>Tensor axis</th>
<th>( \delta ) (ppm)</th>
<th>Orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta_{x} ) (TI)</td>
<td>611</td>
<td>( \delta_{x} ) (TI)</td>
</tr>
<tr>
<td>( \delta_{y} ) (TI)</td>
<td>680</td>
<td>( \delta_{y} ) (TI)</td>
</tr>
<tr>
<td>( \delta_{z} ) (TI)</td>
<td>1329</td>
<td>( \delta_{z} ) (TI)</td>
</tr>
<tr>
<td>( \delta_{\text{iso}} ) (TI)</td>
<td>873.3</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3. Principal axes of the chemical shift tensor of \( ^{205}\text{TI} \) and \( ^{207}\text{Pb} \) in TIPbI\(_{3} \) at 295 K. External standards: 3.4 molar aqueous solution of TI(OOCCH\(_{3}\)) and saturated aqueous solution of Pb(NO\(_{3}\))\(_{2}\).**

![Projection of the crystal structure of TIPbI\(_{3} \) (space group \( D_{2h}^{17} = \text{Cmcm}, Z = 4 \)\([37]\)) along [100].](image)
Fig. 8. Projection of the coordination polyhedron of TI and the directions of the principal axes of the chemical shift tensor. Upper part: Projection along [100]. The TI-atom and the two I(1)-atoms drawn with single circles lie in the paper plane. The double circles for the other I(1)- and the I(2)-atoms indicate, that there are two atoms in each case, one above and one below the paper plane, which forms a mirror plane for the polyhedron. Lower part: Projection along [001]. The TI-atom and the two I(2)-atoms are in the paper plane, which forms a mirror plane for the polyhedron, too. The meaning of the double circles is the same as above.

Table 4. Metal-halogen distances in TlPbI$_3$ after [37].

<table>
<thead>
<tr>
<th>Atom–Atom</th>
<th>Distance/nm</th>
<th>Number of distances in the coordination polyhedron</th>
</tr>
</thead>
<tbody>
<tr>
<td>TI–I(1)</td>
<td>361.4</td>
<td>4</td>
</tr>
<tr>
<td>TI–I(1)</td>
<td>397.1</td>
<td>2</td>
</tr>
<tr>
<td>TI–I(2)</td>
<td>346.7</td>
<td>2</td>
</tr>
<tr>
<td>Pb–I(1)</td>
<td>322.0</td>
<td>4</td>
</tr>
<tr>
<td>Pb–I(2)</td>
<td>318.1</td>
<td>2</td>
</tr>
</tbody>
</table>

$^{29}$Si NMR and the Si–O distances in a single crystal of Mg$_2$SiO$_4$ [45].

Since in that case the frequency of the reference sample (Tetramethylsilane) lies above that of the solid, the highest value of $|\delta^{(29)Si}|$ belongs to the lowest frequency, in contrast to that of $\delta^{(205)TI}$ and $\delta^{(207)Pb}$ in TlPbI$_3$.

In the framework of a superposition model a $\delta^{(203)TI}$ tensor with rotational symmetry around an axis perpendicular to the plane defined by I(2), TI, and I(1) would result for an angle $\alpha$ (I(2)–TI–I(1)) = 90°.

Fig. 9. Projection of the PbI$_6$ octahedron and the directions of the principal axes of the $^{207}$Pb chemical shift tensor. Upper part: Projection along [100]. The Pb- and the two I(1)-atoms lie in the paper plane, which forms a mirror plane for the octahedron. The meaning of the double circles is the same as in Figure 8. Lower part: Projection along [001].

Consideration of the influence of further neighbouring atoms can alter the picture. The slight deviation of the angle $\alpha$ (I(2)–TI–I(1)) from 90° (in TlPbI$_3$ this angle is 83.67°) may be responsible for the deviation of the $\delta^{(205)TI}$ tensor from axial symmetry.

The Pb-atoms occupy the point position 4a with symmetry 2/m. Therefore only one of the principal axes of the $\delta^{(207)Pb}$-tensor coincides with one of the crystal axes (the axis a in TlPbI$_3$). Consequently the two other principal axes are located in the $b$, c-plane. For the rotation of a single crystal around [100] one therefore expects two rotation patterns $\delta^{(207)Pb)} = f(\alpha)$, where $\alpha$ is the rotation angle. Figure 6 shows the angular dependence of $\delta^{(207)Pb)}$ for rotation around [100]. It is seen therefrom that the principal axes of $\delta^{(207)Pb)}$ in the plane (b, c) belong to two symmetry correlated tensors and, in consequence, to two lead atoms located at symmetry correlated points of the point position 4a. The axes form angles of 30° and 120° (tensor 1) and 150° and 60° (tensor 2), respectively, with $b$.

From Figs. 5 and 6 it is obvious that the $\delta^{(207)Pb)}$-tensor is highly anisotropic and possesses almost axial symmetry around $c$. An answer to the question which of the two symmetry correlated tensors belongs to which of the two symmetry correlated...
$\text{PbI}_6$-octahedra (see Fig. 7) may be found by two arguments:

1. From the crystal structure it can be concluded that the $\text{PbI}_6$ octahedra have a pseudofourfold axis along the direction $I^{(21)} - \text{Pb} - I^{(12)}$ (see Figure 9). The four $\text{Pb} - I^{(1)}$ bond length are equal (see Table 4). Therefore, in the first approximation, the $\delta_r(207\text{Pb})$-tensor should be axially symmetric around this axis. This leads to the conclusion that the two tensor axes of almost equal magnitude ($\delta_r(207\text{Pb})$ and $\delta_r(207\text{Pb})$, see Table 3) should be perpendicular to the $\text{Pb} - I^{(2)}$ direction and that the unique axis $\delta_r(207\text{Pb})$ should be parallel to it.

2. The principal axis with the lowest frequency (smallest chemical shift value) $\delta_2(207\text{Pb})$ should be correlated to the shortest $\text{Pb} - I$ distances, in analogy to the results for $\delta(205\text{Tl})$. This leads to $\delta_2(207\text{Pb}) || \text{Pb} - I^{(2)}$.

Both arguments lead to the same result. In Fig. 9 the orientation of the two symmetry correlated $\delta(\text{Pb})$-tensors with respect to the two symmetry related $\text{PbI}_6$ octahedra is depicted. One notes that the idealized assumption $\delta_2(207\text{Pb}) || \text{Pb} - I^{(2)}$ is almost realized. The angle $\angle (\delta_2(207\text{Pb}), \text{Pb} - I^{(2)})$ amounts to 8.7°. The alternative assignment leads to no correlation between structure and tensor orientation and is rejected for the above reasons.

Acknowledgement

We are grateful to the Deutsche Forschungsgemeinschaft for support of this work.