Introduction

The SnX$_3^-$ (X = halogen) is essentially a trigonal pyramid such as isoelectronic SbX$_3$, having lone-pair electrons toward the three-fold axis. In the crystal lattice, however, not only the trigonal pyramid but also square pyramid or octahedral coordination due to halogen bridging appears [1–3]. In a cubic perovskite such as CsSnBr$_3$ [4, 5] and CH$_3$NH$_3$SnBr$_3$, Sn(II) is coordinated octahedrally by Br$^-$ [2]. In these complexes the mainly available bonding-orbitals of Sn(II) are the 5p-orbitals because the 5s-orbital is occupied by a lone-pair and the 5d-energy levels are too high. This situation is called the hypervalent state of Sn(II). The linear X–Sn–X fraction is similar to the I$_3^-$-anion having the three-center-four-electron bond (3c–4e) proposed by Pimentel [6, 7]. From the simple MO approach or halogen NQR-frequency, the 3c–4e bond has been recognized to have a higher ionic character than the normal 2c–2e bond. Indeed, two quite different structures for the I$_3^-$-anion, symmetric and asymmetric, have been found [9, 10]. The structural variety of SnI$_3^-$ stated above could be understood as a deformation of the 3c-4e bond in the three orthogonal directions.

The perovskites CsSnI$_3$ and CH$_3$NH$_3$SnI$_3$ have extremely high electrical conductivity. Most MSnI$_3$ compounds are yellow to orange, but the crystals having perovskite structure are black and have a metallic luster. These anomalous physical properties may be closely related to the linear –I–Sn–I–Sn– chain formed in the perovskite lattice. In this study the structures of the anion and the anomalously high electrical conductivity of the perovskites are discussed on the basis of $^{127}$I-NQR and $^{119}$Sn Mössbauer spectroscopy.

Experimental

SnI$_2$ was prepared by heating stoichiometric amounts of SnI$_4$ and Sn-metal in an evacuated tube at 350 °C for a week and was further purified by a Bridgman technique. All compounds except CH$_3$NH$_3$SnI$_3$ were crystallized from the melt. CH$_3$NH$_3$SnI$_3$ was prepared by a solid state reaction at 200 °C from well powdered CH$_3$NH$_3$I and SnI$_2$ in an evacuated tube. The 4-probe method was employed to measure the electrical conductivity using a single crystal or a pressed powder sample. NQR spectra were observed as a normal 2c–2e bond. Indeed, two quite different structures for the I$_3^-$-anion, symmetric and asymmetric, have been found [9, 10]. The structural variety of SnI$_3^-$ stated above could be understood as a deformation of the 3c-4e bond in the three orthogonal directions.

Key words: NQR, Mössbauer effect, Perovskite compound, Phase transition, Electrical conductivity.
by means of a Matec pulsed spectrometer. The relaxation times $T_1$ were determined by a three pulse method, $180^\circ - \tau - 90^\circ - 180^\circ$ echo. The recovery of the echo intensity could be expressed using a single time constant. $^{119}\text{Sn}$ Mössbauer spectra were recorded at 115 K by means of a constant acceleration type spectrometer using Ca$^{119m}$SnO$_3$ as a radiation source.

## Results and Discussion

### 1. Powder X-Ray Diffraction, DTA, and Electrical Conductivity

According to the structural analysis reported by Mauersberger and Huber [11], SnI$_3$ consists of distorted (SnI$_6$)$_{o}$-octahedra forming double chains along the c-axis (Figure 1A). Thus there are three different bonding for the iodines, i.e. terminal, bridge, and triply bridge iodines (hereafter abbreviated as I(1), I(2) and I(3), respectively). The coordination around Sn(II) is regarded as a square pyramid having one short Sn–I bond (2.941 Å) and four Sn–I bonds on the basal plane (3.197–3.227 Å). The grown CsSnI$_3$ single crystal was black, but it turned to green after grinding. The powder X-ray pattern of this green sample was consistent with that simulated from the orthorhombic CsSnI$_3$ data reported in [11]. RbSnI$_3$ was isomorphous with CsSnI$_3$ (see Table 1); the indexing of the $(hkl)$ reflections was unsuccessful, however, for NH$_4$SnI$_3$ and KSnI$_3$. As will be described later, the $^{127}\text{I}$-NQR spectra for $M = \text{NH}_4$ and Rb resemble to that of CsSnI$_3$, suggesting similar (SnI$_3$)$_{o}$-chains in these crystals. The black crystal of CH$_3$NH$_3$SnI$_3$ showed a cubic perovskite pattern with $a = 6.231$ Å, so that the Sn(II) site has an O$_6$ symmetry with six $3.116$ Å Sn–I bonds. DTA was observed for $M = \text{K, NH}_4$, Cs, and CH$_3$NH$_3$SnI$_3$ in the temperature range 100–450 K. Below $295$ K no heat anomaly was observed in the DTA curves for $M = \text{K, NH}_4$, and Cs, but with increasing temperature exothermic peaks were observed at $342$ K, $416$ K, and $425$ K, respectively. The compounds, except $M = \text{Cs}$, returned to the low temperature phases. The high temperature phase of CsSnI$_3$, however, remained black and slowly returned to the green phases CsSnI$_3$(G) (hereafter the abbreviations (B) and (G) are used for the two phases). The black phase has a perovskite structure similar to CH$_3$NH$_3$SnI$_3$ and is stable if quenched to $77$ K. Hence, $^{127}\text{I}$-NQR, $^{119}\text{Sn}$ Mössbauer spectra and the electrical conductivity were measured for CsSnI$_3$(B) in detail. Part of the NQR and DTA results for $M = \text{Cs}$ and CH$_3$NH$_3$ have been reported previously [3].

Figure 2 shows the electrical conductivity of CsSnI$_3$ and CH$_3$NH$_3$SnI$_3$ as functions of temperature. The pellet sample prepared from CsSnI$_3$(G) showed a semiconductor type behavior below $T_c$ (425 K), but at $T_c$ an increase of the conductivity by four orders of magnitude was observed, associated with the phase transition from CsSnI$_3$(G) to CsSnI$_3$(B). On the other hand, a single crystal of CsSnI$_3$ obtained from the melt was essentially CsSnI$_3$(B), but the conductivity was not so high due to the formation of CsSnI$_3$(G) on the surface. Hence, the conductivity of CsSnI$_3$(B) was measured after heating the single crystal above $T_c$ (see Figure 2). The conductivity for CsSnI$_3$(B) increased gradually with decreasing temperature, such as observed for metals. This extremely high conductivity may be closely related to the perovskite lattice in which infinite linear $–1–\text{Sn}–1–\text{Sn}–$ chains are formed three dimensionally.
2. $^{127}$I-NQR Spectra and Relaxation

Because of the existence of three different bonding schemes, $^{127}$I-NQR was observed over the wide frequency region from 20 to 140 MHz. As Table 2 shows, the $^{127}$I-NQR spectra resembling to each other suggest that the $M = NH_{3}, \text{Rb, and Cs (G)}$ analogues are isomorphous. In the case of KSnI$_3$, more than 8 lines were observed in the range 50–140 MHz, but neither the assignment nor the model structure could be deduced. Perovskite CsSnI$_3$(B), on the other hand, showed extremely broad $v_1 (1/2 \leftrightarrow 3/2)$ transitions with an intensity ratio of 2:1, and the splitting between them decreased with increasing temperature as is shown in Figure 3. These findings, together with the reported powder X-ray diffraction, suggest that a tetragonal distortion takes place already at room temperature [3]. Heat anomalies were also observed in our previous DTA-curves for CsSnI$_3$(B) at 352 and 425 K, but it was not established which anomaly corresponds to the phase transition from tetragonal to cubic. A single $^{127}$I-NQR $v_1$-line was also expected at around 90 MHz for the cubic perovskite CH$_3$NH$_3$SnI$_3$, but not detected.

The asymmetry parameters shown in Table 2 are relatively large even for the terminal iodines, suggesting a large contribution from the lattice to the electric field gradient (egf) at the iodine site. In the first order approximation, however, the quadrupole coupling constant at the iodine is expressed as an imbalance of the iodine 5p-electrons, i.e.

$$
\frac{e^2Q_{\text{obs}}}{e^2Q_{\text{p}}} = \frac{|N_z - (N_y + N_x)/2|}{1},
$$

where $N_x$, $N_y$, and $N_z$ are the populations of the $5p_x$, $5p_y$, and $5p_z$ orbitals, respectively, and $e^2Q_{\text{p}}/h = 2293$ MHz. The Sn–I–Sn bond angles are close to 90° or 180° in all cases. Then (1) reduces to the following equations depending upon the bonding type in Fig. 4, assuming a lone-pair ($N = 2$) for the non-bonding directions:

$$
\begin{align*}
\text{I(1) and I(4)}: & \quad \frac{e^2Q_{\text{obs}}}{e^2Q_{\text{p}}} = |N_z|, \\
\text{I(2)}: & \quad \frac{e^2Q_{\text{obs}}}{e^2Q_{\text{p}}} = |N_x|, \\
\text{I(3)}: & \quad \frac{e^2Q_{\text{obs}}}{e^2Q_{\text{p}}} = |N_y|.
\end{align*}
$$

Table 2. $^{127}$I-NQR parameters for MSnI$_3$ at 77 and 293 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$v_1$/MHz</th>
<th>$v_2$/MHz</th>
<th>$e^2Q_{\text{p}}h^{-1}$/MHz</th>
<th>$\eta$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$SnI$_3$</td>
<td>20.42</td>
<td>36.89</td>
<td>125.0</td>
<td>0.290</td>
<td>I(3)</td>
</tr>
<tr>
<td></td>
<td>52.88 (52.59)</td>
<td>99.35 (96.50)</td>
<td>334.5 (326.2)</td>
<td>0.225 (0.267)</td>
<td>I(2)</td>
</tr>
<tr>
<td></td>
<td>72.59 (72.58)</td>
<td>122.03</td>
<td>418.6</td>
<td>0.394</td>
<td>I(1)</td>
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<tr>
<td>RbSnI$_3$</td>
<td>23.42</td>
<td>40.66</td>
<td>138.7</td>
<td>0.350</td>
<td>I(3)</td>
</tr>
<tr>
<td></td>
<td>55.26 (54.58)</td>
<td>97.73 (95.74)</td>
<td>332.3 (326.0)</td>
<td>0.324 (0.326)</td>
<td>I(2)</td>
</tr>
<tr>
<td></td>
<td>78.34 (76.58)</td>
<td>135.46 (134.69)</td>
<td>462.4 (458.5)</td>
<td>0.356 (0.332)</td>
<td>I(1)</td>
</tr>
<tr>
<td>CsSnI$_3$(G)</td>
<td>25.30</td>
<td>43.10</td>
<td>147.5</td>
<td>0.376</td>
<td>I(3)</td>
</tr>
<tr>
<td></td>
<td>58.25 (56.86)</td>
<td>99.50 (97.42)</td>
<td>340.4 (333.1)</td>
<td>0.373 (0.369)</td>
<td>I(2)</td>
</tr>
<tr>
<td></td>
<td>81.29 (79.59)</td>
<td>138.70 (137.64)</td>
<td>474.5 (469.8)</td>
<td>0.374 (0.356)</td>
<td>I(1)</td>
</tr>
<tr>
<td>CsSnI$_3$(B)</td>
<td>88.6 (88.2)</td>
<td>94.2 (90.5)</td>
<td>591 (588)</td>
<td>0 (assumed)</td>
<td>I(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>628 (603)</td>
<td>0 (assumed)</td>
<td>I(4)</td>
</tr>
</tbody>
</table>

* Values for 293 K in brackets.

$^b$ Calculated assuming $\eta = 0$. 

Fig. 2. Temperature dependence of the electrical conductivity of CsSnI$_3$ and CH$_3$NH$_3$SnI$_3$. 

Table 2. $^{127}$I-NQR parameters for MSnI$_3$ at 77 and 293 K.
Table 4. $^{119}$Sn Mössbauer parameters for MSnI$_3$ at 115 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>IS</th>
<th>QS</th>
</tr>
</thead>
<tbody>
<tr>
<td>KSnI$_3$</td>
<td></td>
<td>3.94</td>
<td>0.42</td>
</tr>
<tr>
<td>NH$_4$SnI$_3$</td>
<td>square pyramid</td>
<td>4.06</td>
<td>0.26</td>
</tr>
<tr>
<td>RbSnI$_3$</td>
<td></td>
<td>4.02</td>
<td>0.37</td>
</tr>
<tr>
<td>CsSnI$_3$(G)</td>
<td>square pyramid</td>
<td>4.03</td>
<td>0.37</td>
</tr>
<tr>
<td>CsSnI$_3$(B)</td>
<td>octahedron</td>
<td>3.85</td>
<td>0</td>
</tr>
<tr>
<td>CH$_3$NH$_3$SnI$_3$</td>
<td>octahedron</td>
<td>3.84</td>
<td>0</td>
</tr>
</tbody>
</table>

* Quadrupole splittings were calculated assuming the linewidth parameter = 0.94 mm/s, which was deduced from perovskite CH$_3$NH$_3$SnI$_3$.

Table 4 summarizes the $^{119}$Sn Mössbauer parameters, quadrupole splitting (QS) and isomer shift (IS), at 115 K. In order to see the correlation between Mössbauer parameters and their structures, Fig. 7 plots QS against IS. From the standpoint of the spherical coordination in the perovskite lattice, a high IS value in the order of 4.05 mm s$^{-1}$ is expected. The observed IS for the perovskite compounds, however, is much smaller than expected. According to Parish, IS depends directly on the valence-shell s-population and indirectly on the p-population by shielding, and is empirically expressed as [12]

$$\text{IS} = 2.7 N_s - 0.15 N_p,$$

where $N_s$ and $N_p$ are the population of the tin 5s- and 5p-orbitals. This unusually small IS is consistent with the band structure proposed by Clark et al. [13] for the interpretation of the semi-metallic CsSnBr$_3$, i.e. (3) suggests the donation of 0.07 s-electrons into a conduction band for CsSnI$_3$(B) and CH$_3$NH$_3$SnI$_3$.

3. $^{119}$Sn Mössbauer Effect

Figure 6 shows the $^{119}$Sn Mössbauer spectra for CsSnI$_3$(G) and CsSnI$_3$(B), which were assigned to Sn(II) atoms with square pyramidal and regular octahedral coordination, respectively. The $^{119}$Sn Mössbauer spectrum corresponding to the square pyramidal coordination was essentially a doublet, but the splitting is smaller than 1/2 of the respective linewidth. Consequently, each doublet was analyzed having the same linewidth as that of the perovskite CH$_3$NH$_3$SnI$_3$. Table 4 summarizes the $^{119}$Sn Mössbauer parameters, quadrupole splitting (QS) and isomer shift (IS), at 115 K. In order to see the correlation between Mössbauer parameters and their structures, Fig. 7 plots QS against IS. From the standpoint of the spherical coordination in the perovskite lattice, a high IS value in the order of 4.05 mm s$^{-1}$ is expected. The observed IS for the perovskite compounds, however, is much smaller than expected. According to Parish, IS depends directly on the valence-shell s-population and indirectly on the p-population by shielding, and is empirically expressed as [12]

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vibrations, respectively. The slope of $\log(T_1)/\log(\text{Temp})$ in Fig. 5 is expected to be $-2$ if only the second term contributes to the relaxation similar to the system containing $I = 3/2$ nuclei. Experimentally determined slopes are $1.91 \pm 0.05$ and $1.20 \pm 0.5$ for Cs(G) and Cs(B), respectively. These values suggest that the relaxation in Cs(B) is mainly governed by conduction electrons which seems to localize on the probe iodine. If the contribution from the second term, $(1/T_1)_{\text{ vib}}$, is subtracted assuming parameters obtained for Cs(G), the slope reduces to 1.01, which agrees well with the theoretical expectation for electronic conductors. The deviation from this line above 250 K is probably due to the phase transition from tetragonal to cubic.