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X-ray study of the incommensurate phase of $TlInS_2$

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Abstract. The successive structural phase transitions in the layer compound $TlInS_2$ have been studied using single-crystal x-ray diffraction. The intermediate phase between 194 K and 214 K is found to be incommensurate; the satellite maps show that the modulation mode which characterizes the intermediate phase has $\boldsymbol{q}_i = (\delta, 0, 0.25)$ ($\delta \approx 0.044$). It is shown that the previously reported satellite reflections at $\boldsymbol{q} = (\delta, \delta, 0.25)$ are ascribable to twins. A structure model is presented for the incommensurate phase. In the low-temperature phase below 197 K, the satellite reflections are shifted to a commensurate position, $\boldsymbol{q}_c = (0, 0, 0.25)$.

1. Introduction

$TlGaSe_2$ and $TlInS_2$ are ternary layer compounds which show semiconducting properties. The ferroelectric phase transitions in these compounds have been studied for more than two decades. Submillimetre spectroscopies, and IR and Raman studies have shown that $TlGaSe_2$ and $TlInS_2$ undergo successive phase transitions accompanied by soft modes [1–4]. Their crystal structure is characterized by metal–chalcogen layers formed of corner-connected tetrahedra, such as $GaSe_4$ and InS_4 [5, 6]. Monovalent Tl ions are located, between the metal–chalcogen layers, linearly along the channels in the [1, 1, 0] and [1, −1, 0] directions. The prototypic unit cell is made up of two such layers, where the upper layer is shifted a quarter of a unit along the [1, 1, 0] and [1, −1, 0] directions. A monoclinic unit cell is usually assigned to this crystal, but, as described below, it has a pseudo-tetragonal symmetry.

X-ray and neutron scattering studies have shown that the low-temperature ferroelectric phase has a fourfold-commensurate structure; the satellite reflections are observed at $\boldsymbol{q}_c = (0, 0, 0.25)$ [7, 8]. It is also reported that the intermediate phase is incommensurate; the satellite reflections are reported to appear at $\boldsymbol{q} = (\delta, \delta, 0.25)$ (δ is reported as 0.012 for $TlInS_2$ [7] and 0.02 for $TlGaSe_2$ [8]). The detailed structure of the incommensurate phase has, however, not been reported yet.

The present study is aimed at clarifying the nature of the successive phase transitions in the thallium compounds. In this paper, we report the results of low-temperature x-ray investigations of $TlInS_2$. Our attention is focused on the structure of the intermediate phase which is reported to exist between 216 K and 200 K [3].

2. Experimental procedure

Single-crystal samples of $TlInS_2$ are grown by the Bridgman method. Stoichiometric amounts of the elements (99.999%) are sealed in an evacuated quartz tube. The sample is melted

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at 850 °C and then solidified by a slow cooling. The crystals obtained are transparent and dark yellow, and are cleaved easily in the *a–b* plane. In order to check the phase transition points, the temperature dependence of the dielectric constant is measured using a Hewlett–Packard capacitance bridge, 4270A. A small sample is cut normal to the [1, 1, 0] axis. Silver paint is used as the electrode material. The measurements are made during gradual cooling (0.2 K min^{-1}) at four fixed frequencies, 1 kHz, 10 kHz, 100 kHz and 1 MHz.

The x-ray diffraction data are collected on a Huber four-circle diffractometer. Graphite-monochromated Cu and Mo Kα radiations are used. A small cleaved crystal is carefully checked for twins by taking precession photographs. The crystal is then mounted on a goniometer head and set in a stream of cold nitrogen gas. The temperature of the crystal is kept constant within 0.2 K by a PID temperature controller.

3. Results and discussion

The unit-cell parameters deduced from the x-ray diffraction angles are $a = 10.90$ Å, $b = 10.94$ Å, $c = 15.18$ Å and $\beta = 100.21°$ (space group $C2/c$, $Z = 16$ at 290 K). A triclinic unit cell can also be chosen, with $a' = b' = a/\sqrt{2}$, $c' = c$, $\alpha' = \beta' = 97°$ and $\gamma' = 90°$ ($Z = 8$), which has a pseudo-tetragonal symmetry.

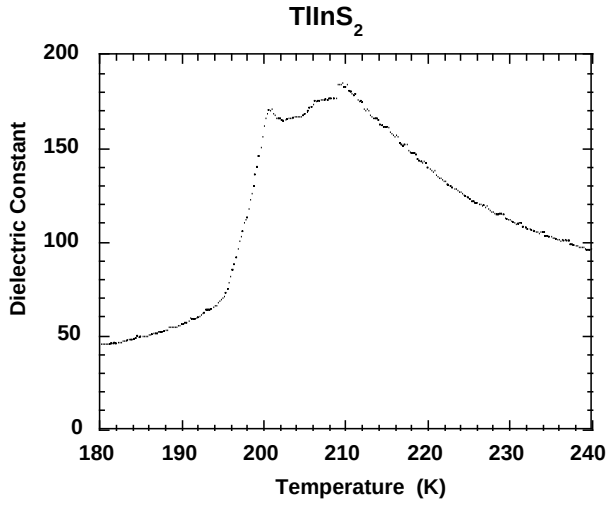


Figure 1. The temperature dependence of the real part of the dielectric constant in $TlInS_2$ measured along the [1, 1, 0] axis. The peak at 210 K and the shoulder at 197 K correspond to transitions to the intermediate- and the lowest-temperature phases, respectively. (See the text.)

Figure 1 shows the temperature dependence of the real part of the dielectric constant measured along the [1, 1, 0] axis. Upon cooling, the dielectric constant shows maxima at two points, 209 K and 200 K, and a shoulder at 197 K, suggesting successive phase transitions. In the paraelectric phase, the dielectric constant can be fitted by the Curie–Weiss curve. At higher temperatures, however, owing to the semiconducting nature of the crystal, the dc conductivity increases and the dielectric constant deviates from the Curie–Weiss curve. The frequency dependence of the real part of the dielectric constant is small, while the imaginary part has some dependent parts derived from the dc conduction.

Figure 2 shows the integrated intensity of the diffraction peaks near (4, 0, 5.25), plotted against temperature. When the sample is cooled below about 214 K, satellite reflections appear.

In the temperature range between 214 K and 197 K, the satellite intensity increases almost linearly as the temperature is decreased, $I \propto 214 - T$. Below about 197 K, the satellite intensity increases steeply, suggesting a second transition to the low-temperature phase.

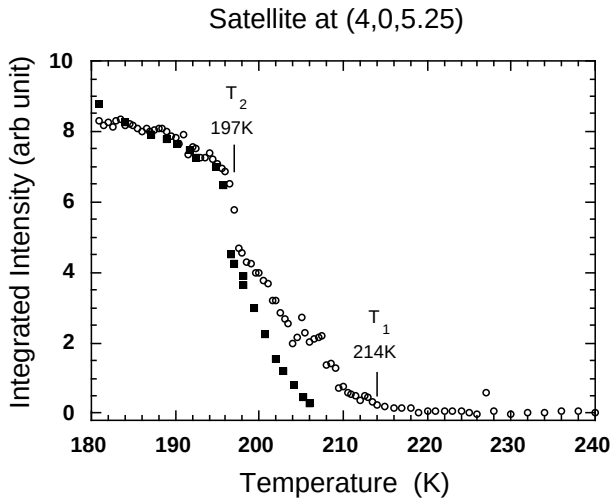
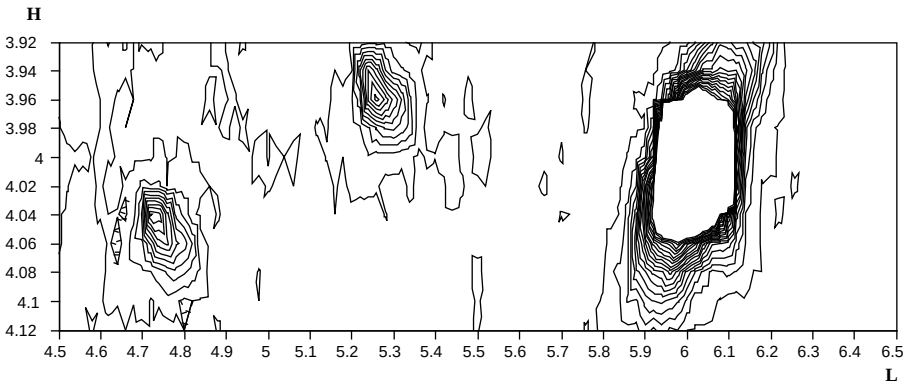


Figure 2. The temperature dependence of the integrated intensity of the satellite peak in $TlInS_2$, measured around the (4, 0, 5.25) Bragg point. The full squares show the data for the spontaneous polarization [2] normalized at 85 K.

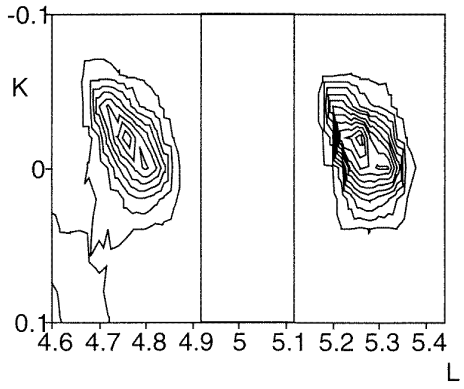
In a recent study of $TlInS_2$, Allakhverdiev *et al* observed a complicated nature of the transitions [4]. They reported that the dielectric constant shows a shoulder at 195 K and three peaks at 201 K, 206 K and 216 K. They assigned the shoulder at 195 K to the lock-in transition to the commensurate phase; the peaks at 201 K and 206 K to incomplete lock-in transitions; and the peak at 216 K to the normal-to-incommensurate phase transition [4]. They also reported that the transition process is a little sample dependent. From comparing figures 1 and 2, we regard the shoulder at 197 K (figure 1) as corresponding to the lock-in transition, but not the peak at 200 K.

In order to search for the modulation vector which characterizes the intermediate phase, the diffraction intensity is scanned step by step at meshes in the $(h, 0, l)$, $(0, k, l)$ and (h, h, l) zones. Figure 3(a) shows the contour map taken around the Bragg points (4, 0, 5) and (4, 0, 6) scanned in the a^*–c^* plane (note that the (4, 0, 5) main reflection is absent because of the glide symmetry c). The satellite positions are shifted along the a^*-direction suggesting that the intermediate phase is incommensurate. Figure 3(b) shows the intensity map of the satellites scanned in the b^*–c^* plane. Figures 3(a) and 3(b) clearly show that the satellites are located at $\boldsymbol{q} = (-0.044, 0, 0.25)$ and $(0.044, 0, -0.25)$. Although the intermediate phase is incommensurate, the wave vector is different from that given in previous papers, where the satellites are reported to appear at $\boldsymbol{q} = (\delta, \delta, 0.25)$ (δ is reported as 0.012 in reference [7]). We think that the previously reported satellite diffraction at $\boldsymbol{q} = (\delta, \delta, 0.25)$ is ascribable to twins contained in the crystal, where the two axes a and b are exchanged and mixed. The satellite intensity increases as the temperature is decreased. Throughout the intermediate phase, however, the direction of the modulation is almost temperature independent.

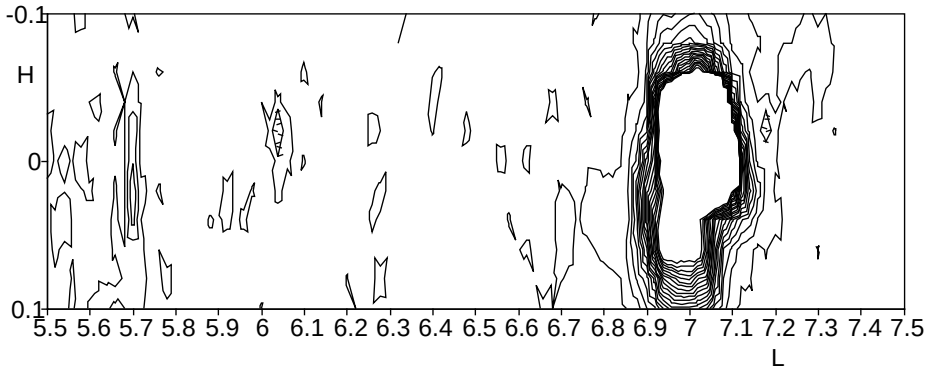
Figure 3(c) shows the contour map taken in the a^*–c^* plane around the (0, 4, 6) and (0, 4, 7) Bragg points; owing to the above-mentioned pseudo-tetragonal symmetry, the two main reflections (4, 0, 6) and (0, 4, 7) are equivalent in the high-temperature phase. We notice



(a)



(b)



(c)

Figure 3. Diffraction intensity maps for the incommensurate phase of $TlInS_2$: taken around the (4, 0, 5) and (4, 0, 6) Bragg points: (a) scanned in the a^*–c^* plane; (b) scanned in the b^*–c^* plane; (c) scanned in the a^*–c^* plane around the (0, 4, 6) and (0, 4, 7) Bragg points. Note that in (a) the main peak at (4, 0, 5) is absent and the satellite peak at $l = 4.75$ is shifted along the a^*-axis by about 0.044 while the peak at $l = 5.25$ is shifted by -0.044. Also note that in (c) satellites are not observed (a sharp narrow line at around (0, 4, 5.75) is attributed to multiple scattering).

that the satellites are not observed in the $(0kl)$ zone: this is extinction rule (i) (see figure 3(c)). We find that in the $(h0l)$ zone, the satellites appear only around the main reflections having indices $h = 4m$ and $l = 2n + 1$ (where m and n are integers): this is extinction rule (ii) (see figure 3(a)). We find also a third extinction rule, rule (iii): the satellite reflections are absent in the $(0, 0, l)$ line.

In a recent paper [9], a binary compound TlS was reported to undergo similar phase transitions. At room temperature, monoclinic TlS is ferroelectric and the superlattice reflections are observed at (0, 0, 0.25). The structure is, therefore, isomorphic with that of the low-temperature phase of the ternary compounds. Upon heating, TlS exhibits successive phase transitions. It is reported that the high-temperature phase is paraelectric and the intermediate phase between 345 K and 320 K is incommensurate, where the satellite reflections appear at $\boldsymbol{q} = (-0.04, 0, 0.25)$ and $(0.04, 0, -0.25)$, but not at $\boldsymbol{q} = (\delta, \delta, 0.25)$ [10].

The structural phase transition in $TlInS_2$ can be ascribed to small displacements of atoms from the positions that they occupy in the high-temperature high-symmetry phase. Since the dielectric constant measured along the c-axis shows little anomaly at the phase transition points, we can expect the relevant displacements to be in the a–b plane. The last extinction rule, rule (iii), also suggests that the atomic displacements are in the a–b plane. The first extinction rule, rule (i), suggests that the displacements are parallel to the a-axis.

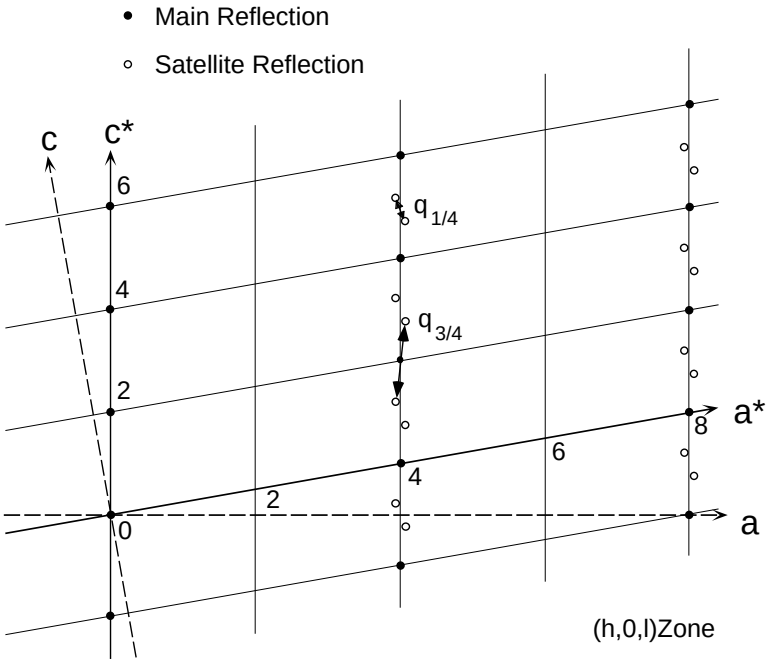


Figure 4. Diffraction spots observed in the incommensurate phase of $TlInS_2$. The vectors $\boldsymbol{q}_{1/4}$ and $\boldsymbol{q}_{3/4}$ show the modulation waves at $\boldsymbol{q}_{1/4} = (-0.044, 0, 0.25)$ and $\boldsymbol{q}_{3/4} = (0.044, 0, 0.75)$.

The diffraction pattern in figure 4 shows intuitively that the modulation vector which characterizes the intermediate phase is not of the fundamental $\boldsymbol{q}_{1/4}$-type, but of the third-harmonic $\boldsymbol{q}_{3/4}$-type. Let us discuss this point a little further [11]. For the wave vector $\boldsymbol{q} = (\delta, 0, 0.25)$, the little group contains the c-glide plane in addition to the identity. Hence the modulation displacements have either even or odd character with respect to $\boldsymbol{c}$. Take the

modulated displacements as sinusoidal:

$$\boldsymbol{u}_{lk} = \boldsymbol{A}_k \sin(\boldsymbol{q}\cdot\boldsymbol{r}_{lk} + \Phi_k). \tag{1}$$

Assuming a c-glide (atoms at $\boldsymbol{k}$: (x, y, z) and $\boldsymbol{k}'$: $(x, -y, 1/2 + z)$), the structure factor of the mth-order satellite reflection is given by

$$F_m(\boldsymbol{Q}) = \delta(\boldsymbol{Q} - m\boldsymbol{q} - \boldsymbol{G}) \sum_{k,k'} f_k J_m(\boldsymbol{Q}\cdot\boldsymbol{A}_k)[\exp(\mathrm{i}m\Phi_k)\exp(2\pi\mathrm{i}[hx_k + ky_k + lz_k])$$
$$+ \exp(\mathrm{i}m\Phi_{k'})\exp(2\pi\mathrm{i}[hx_k - ky_k + l(1/2 + z_k)])] \tag{2}$$

where $\boldsymbol{G}$ is the reciprocal-lattice vector, f_k is the form factor of the kth and k'th atoms, J_m is the Bessel function [12].

For modulated displacements that are even with respect to $\boldsymbol{c}$, we have $\Phi_{k'} = \Phi_k$, while $\Phi_{k'} = \Phi_k + \pi$ for odd displacements. Hence for the $(h0l)$ zone reflections $\boldsymbol{Q} = m\boldsymbol{q} + \boldsymbol{G}_{hol}$,

$$F_m(\boldsymbol{Q}) = \sum_{k,k'} f_k J_m(\boldsymbol{Q}\cdot\boldsymbol{A}_k)\exp(\mathrm{i}m\Phi_k)\exp(2\pi\mathrm{i}[hx_k + lz_k])(1 + (-1)^p) \tag{3}$$

with $p = l$ or $l + m$ depending upon the parity of the displacements with respect to $\boldsymbol{c}$. For even displacements, the satellites ($m = 1, 2, 3, \ldots$) follow the same extinction rule as the parent fundamental reflection ($m = 0$), whereas for odd displacements, the odd-order satellites

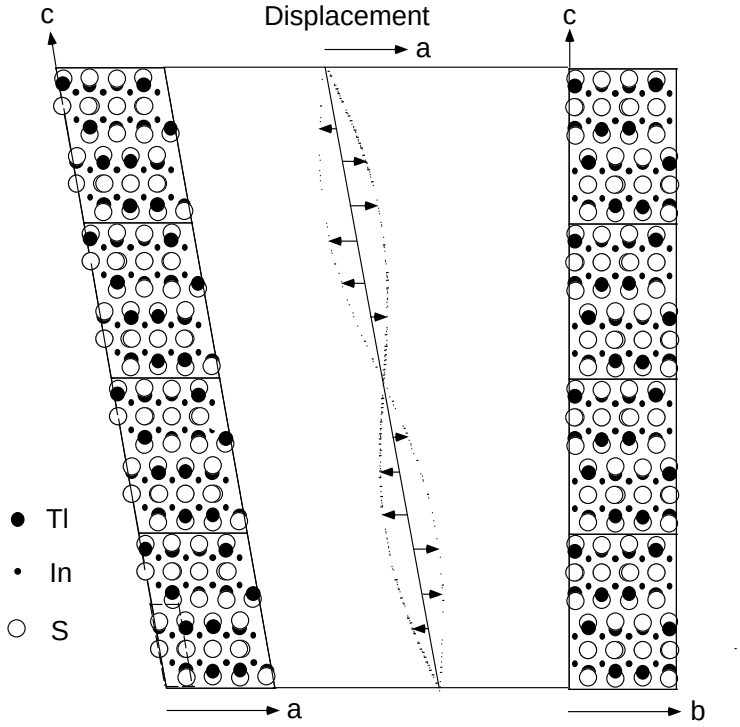
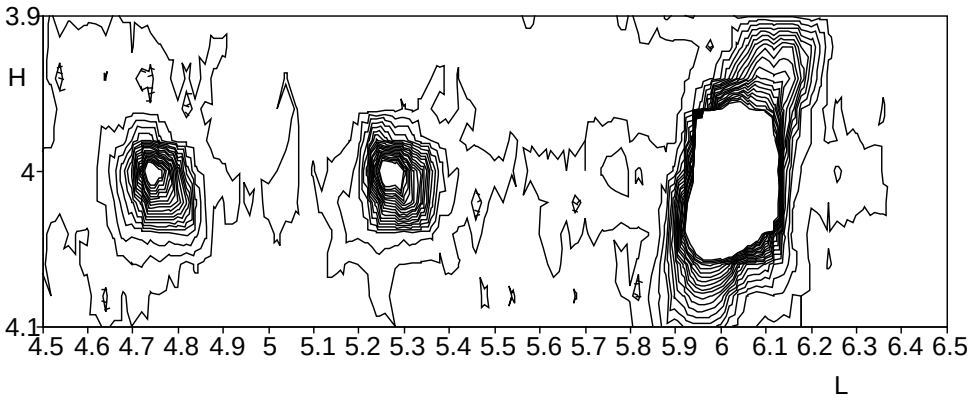


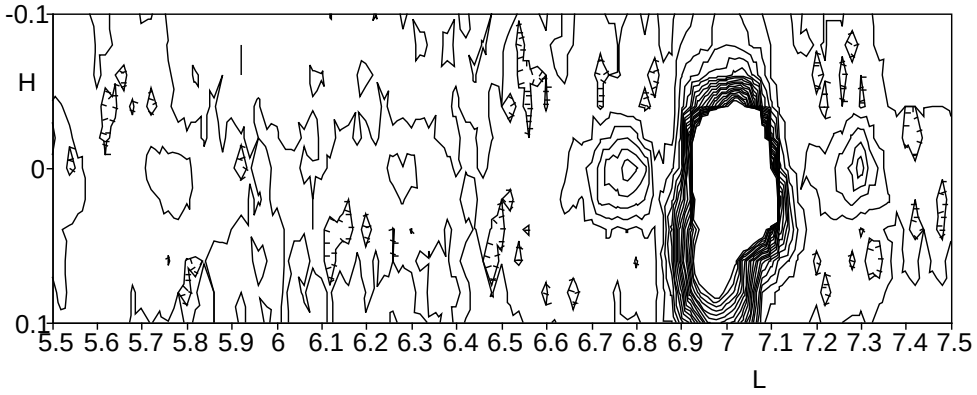
Figure 5. A schematic drawing of the unit-cell stackings in $TlInS_2$. The curves and arrows in the central part show the displacement mode in the incommensurate phase. The displacements are of odd parity with respect to the c-glide (see the text). The dotted lines at the bottom of the left-hand stacking show the structure unit which gives rise to the incommensurate reflections. Note that in the projection along the a-axis (right) the atoms show the same arrangement as in the projection along the b-axis (left).

($m = 1, 3, \ldots$) are present, and the fundamental and even-order satellites are extinct. This latter case corresponds to the observed experimental situation (extinction rule (ii)); that is, the atoms connected by the c-glide symmetry move in antiphase.

Figure 5 shows the displacement mode, schematically. The displacements are of optical type and composed of a fundamental wave over the four unit cells along the c-axis. We notice that the mode corresponds to the third harmonic of the acoustic type, $\boldsymbol{q}_{3/4}$. The extinction rule (ii) also shows that the basic motif which gives rise to the incommensurate diffraction is not the usual unit-cell structure but a small unit shown in figure 5. It has a $1/4 \times 1 \times 1/2$ volume of the usual unit cell. This means that the displacements are uniform in the a–b plane, and ions with the same z-coordination will move together.



(a)



(b)

Figure 6. Diffraction intensity maps for the commensurate phase of $TlInS_2$: (a) taken around the (4, 0, 5) and (4, 0, 6) Bragg points; (b) taken around the (0, 4, 6) and (0, 4, 7) Bragg points. Note that in (a) the superlattice reflections are stronger at $\boldsymbol{q}_{3/4} = (0, 0, \pm 0.75)$, while in (b) the reflections are stronger at $\boldsymbol{q}_{1/4} = (0, 0, \pm 0.25)$.

Below about 197 K, the satellites are locked to $\boldsymbol{q}_c = (0, 0, \pm 0.25)$, suggesting a phase transition to the fourfold-commensurate structure (see figures 6(a) and 6(b)). In this phase, the extinction rules (i) and (ii) are broken, and only the third rule, rule (iii), survives. In the

low-temperature phase, therefore, the polarization vector is no longer parallel to the a-axis. The contour map taken in the a–c plane (figure 6(a)) shows that the superlattice intensity is stronger at the positions $\boldsymbol{q}_{3/4} = (0, 0, \pm 0.75)$ than at $\boldsymbol{q}_{1/4} = (0, 0, \pm 0.25)$. We notice that the weak peaks at $\boldsymbol{q}_{1/4}$ are attributable to the third harmonic of the modulation wave at $\boldsymbol{q}_{3/4}$, since $\mathrm{mod}(3 \times 3/4, 1) = 1/4$.

The contour map taken around (0, 4, 7) (figure 6(b)) shows that the satellite diffractions at $\boldsymbol{q}_{1/4} = (0, 0, \pm 0.25)$ are stronger than those at $\boldsymbol{q}_{3/4} = (0, 0, \pm 0.75)$. From a symmetry consideration similar to that described above, the displacements along the b-axis are found to be of even-type modulation, i.e., of the fundamental acoustic type. They can, however, be third harmonics of the mode observed along the a-axis at $\boldsymbol{q} = 3/4$.

The incommensurate phase transitions in the thallium compounds have been discussed by Gashimzade *et al* [13], using the Landau theory. Let us consider the phase sequence from the phenomenological viewpoint. Crystals of the $TlGaSe_2$ family have the space group $C2/c$. Since the representation at $\boldsymbol{q}_{1/4} = (0, 0, \pm 0.25)$ is two dimensional, there are two components of the order parameter, $\boldsymbol{Q}$ and $\boldsymbol{Q}^*$, which give rise to the quadrupling of the unit cell. The expansion of the Landau free energy is given as [10]

$$\Psi(x) = \frac{\alpha}{2} Q Q^* + \frac{\beta}{4}(Q Q^*)^2 + \mathrm{i}\frac{\delta}{2}\left(Q\frac{\mathrm{d}Q^*}{\mathrm{d}x} - Q^*\frac{\mathrm{d}Q}{\mathrm{d}x}\right) + \frac{\kappa}{2}\frac{\mathrm{d}Q}{\mathrm{d}x}\frac{\mathrm{d}Q^*}{\mathrm{d}x} + \frac{\gamma}{2}(Q^8 + Q^{*8}) + \mathrm{i}\xi(Q^4 - Q^{*4})P + \frac{\eta}{2} Q Q^* P^2 + \frac{P^2}{2\chi_0} - PE \tag{4}$$

where $\alpha = \alpha_0(T - T_0)$, β and $\kappa > 0$, and P is the polarization along the b-axis. The third term is the Lifshitz gradient invariant. The fifth term is the lock-in energy which stabilizes the commensurate phase. The sixth and seventh terms are the anisotropic and isotropic couplings between the order parameter and the polarization. The Lifshitz term leads to a spatially modulated phase. Here, the modulation is taken along the a-axis. From symmetry considerations, it could also be taken along the c-axis as Gashimzade *et al* did [11], but it cannot be taken along the b-axis. The present result is, therefore, consistent with the theoretical prediction.

We note that the temperature dependence of the satellite intensity I is similar to that of the spontaneous polarization P reported in reference [2] (see figure 2). The intensity I is proportional to the square of the order parameters $\boldsymbol{Q}$ and $\boldsymbol{Q}^*$. From the above free-energy expansion, however, we see that P is the secondary parameter and is proportional to the fourth power of the order parameters $\boldsymbol{Q}$ and $\boldsymbol{Q}^*$. Further precise data for I and P are needed, in order to decide whether P is proportional to the fourth power of the order parameter or not. The experimental fact that the polarization P persists above the commensurate–incommensurate transition point [2, 4] may lead to another interpretation: that the intermediate phase is a mixture of the high-temperature and the low-temperature phases.

In this study, the modulation vector in the incommensurate phase of $TlInS_2$ has been identified. At present, unfortunately, there are no structural data available for the incommensurate phase in the thallium compounds. For the low-temperature commensurate phase of TlS, Nakamura and Kashida presented a structural model, where monovalent Tl ions and apical S ions are assumed to move normal to the channel directions [1, 1, 0] and [1, −1, 0] in antiphase [14]. The displacements are assumed to be in the form of a sinusoidal wave propagating along the c^*-axis. The present results for the incommensurate phase of $TlInS_2$ show that the displacement vector is in the a-axis direction, and also that the modulation wave is not of the fundamental type but is of the optical type. Further detailed studies, of compounds including TlS, $TlInS_2$ and $TlGaSe_2$, are now in progress in order to clarify such points.

Acknowledgment

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