PHONON SYMMETRIES AND PHASE TRANSITION IN TlSe AND $TlInSe_2$

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The symmetry and atomic displacements corresponding to each phonon have been derived from the calculations of the phonon band structure of TlSe and $TlInSe_2$ chain compounds, which belong to the same family of materials. It is shown that at least acoustic branches along Δ-symmetry line are, for the most part, Einstein-like and their frequency is a weak function of the wave-vector. Anti-crossing between acoustic and low-frequency optic modes along Γ- T direction of the Brillouin zone is found to be similar to that observed in thermoelectric Ba-Ni-Ge clathrates. The found symmetry-forbidden crossing on A-symmetry line between the two-fold degenerated low-frequency phonon modes with A_5 symmetry is vanishing in $TlInSe_2$ in the point with the wave vector of $0.67Å^{-1}$ along the Γ-H-T direction of the Brillouin zone. On the other hand, a kink transforming into a gap-like structure with decreasing temperature has been observed at the same wave-vector for the uppermost valence band of $TlInSe_2$, accessed by angle-resolved photo-emission spectroscopy at SPRING-8 facility (Japan). Both theoretical and experimental data obtained are evident of an incommensurate phase transition due to pseudo-Jahn-Teller effect in $TlInSe_2$.

1. INTRODUCTION

The ternary Tl-contained compounds, $TlMeX_2$, crystallize either into a tetragonal chain structure (MeX = TlSe, InSe, InTe, GaTe) with space group D_{4h}^{18} [1] or into a monoclinic layered structure (MeX= GaSe, GaS, InS) with space group C_{2h}^{6} [2]. In either case the main building blocks are the MeX_4 tetrahedrons arranged into the chains or layers and the Tl-atoms positioned between these chains or layers. Both structures are low-dimensional and can transform into one another under the proper conditions such as, for example, 2Gpa and 873K for $TlGaSe_2$ [2].

The most interesting properties, which promise novel applications in MEMS (micro-electro- mechanical systems) and other devices are giant thermoelectric power [3] and giant thermoelastic effect [4], both are believed to be an attribute of a wide-range incommensurate (modulated) phase emerging in $TlMeX_2$ in the course of the subsequent phase transitions.

Our attention has been attracted to $TlInSe_2$ whose superior thermoelectric and thermoelastic properties have already been verified in an experimental way [3,4]. Concerning the nature of phase transitions, which eventually lead to these properties, the situation is not completely clear. According to the angle-resolved electron photoemission spectroscopy (ARPES) of $TlInSe_2$ [5,6], in a certain arbitrary point on the A-line of the Brillouin zone (BZ) the uppermost valence band exhibits a kink structure that transforms into a gap-like structure upon farther temperature decrease. On the other hand, the available experimental data on heat capacity of $TlInSe_2$ [7-10] are rather ambiguous regarding the clear manifestations of phase transition. The heat effects (if any), accompanying the transition, are small and indicative of the dependence of the obtained results on the thermal history of the measured samples [8, 10]. In connection with this, we consider it important to mention that memory effects are inherent in incommensurate phases and that our very recent studies of the negative differential resistance, reported earlier for all chain $TlMeX_2$ [11-13], have disclosed its strong history dependence that was not mentioned before. According to the works [11-13], non-linear electric properties of all chain $TlMeX_2$ (including $TlInSe_2$) have thermal nature.

In this work we report the symmetry and dispersion of the phonons, as well as atomic displacements leading to the low-frequency phonons near $0.67Å^{-1}$ wave vector along the BZ direction parallel to the chains of TlSe and $TlInSe_2$. We also discuss the possible nature of incommensurate phase transition in $TlInSe_2$. All details concerning the calculations of the phonon band structure of TlSe and $TlInSe_2$ can be found in our recent work [14].

2. PHONON SPECTRA AND SYMMETRIES

In TlSe or $TlInSe_2$ the full vibration representation consists of 24 modes and is given, depending on the position (Γ-point, T-point, Δ-line, A-line etc.) of the wave-vector in the BZ, as

$\Gamma_{vib}=\Gamma_1+2\Gamma_2+\Gamma_3+2\Gamma_4+3\Gamma_5+\Gamma_6+3\Gamma_9+4\Gamma_{10}$

$T_{vib}=T_1+T_2+T_3+3T_4+3T_5+T_6+T_7+2T_9+4T_{10}$

$\Delta_{vib}=6\Delta_1+8\Delta_2+4\Delta_3+6\Delta_4$

$A_{vib}=4A_1+2A_2+A_3+3A_4+7A_5$

Here the irreducible representations Γ_5, Γ_{10}, T_5 , T_{10}, and A_5 are two-dimensional, while the others are one-dimensional.

Since phonon symmetries in the obtained phonon band structures of TlSe and $TlInSe_2$ [15] were not specified, here we give these symmetries for each phonon branch shown in

Fig.1 for normal (non-modulated) phases of TlSe (Fig.1a) and $TlInSe_2$ (Fig.1b). For TlSe ($Tl^{1+}Tl^{3+}Se_2$) and $TlInSe_2$ the pictures of phonon dispersion and symmetries are very similar. This is seen from Fig.2a (TlSe) and Fig.2b ($TlInSe_2$), which reproduce the results for low-frequency part of the phonon spectra along the BZ –directions, Δ and A. Note that the results of calculations of phonon dispersion across the BZ of TlSe are in a good agreement with the inelastic neutron scattering (INS) data [15], as we have shown previously [14]. Therefore we believe that phonon band structures we obtained for TlSe and $TlInSe_2$ are quite reliable.

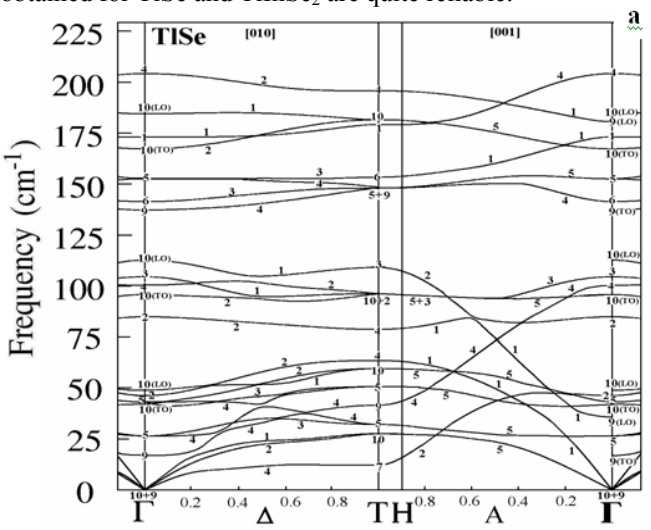

Fig.1 Band structure of TlSe (a) and $TlInSe_2$ (b) in the directions perpendicular (Δ) and parallel (A) to the chains. Numbers on phonon curves show phonon symmetries.

Comparison shows consistence between the phonon symmetries obtained in this work and the phonon symmetries given by Vakhrushev et al [15] for low-frequency part of the phonon spectra of TlSe. The only exception is the mode A_2 (Fig. 2a) compatible with T_7 symmetry in T-point. Although INS data [15] in the relevant frequency range are not detailed enough for unambiguous conclusions, one may think that, in fact, above mode has A_4 rather than A_2 symmetry. Since A_4-symmetry is also compatible with T_7 symmetry in T-point, we leave the matter for more detailed experimental examination.

While acoustic phonons along Δ-line, which is perpendicular to the chains and connects the centre (Γ) of the BZ and surface point T, correspond to one-dimensional irreducible representations (A1 to Δ_4, A2 to Δ_2, and A3 to Δ_1), only LA- mode along A-line, which is parallel to the chains, connects Γ and surface point T' equivalent to T [6], and includes edge point H of the BZ, is described by one-dimensional representation (A_1). In the later case the TA-mode is two-fold degenerated and corresponds to the two-dimensional irreducible representation A_5 (Fig. 2). Especially for the acoustic modes A1 and A2, the slopes of the linear sections in the neighbourhood of the BZ centre is small and so would be sound velocities and rates of heat transfer along the direction perpendicular to the chains. Besides, all acoustic branches along Δ-direction are for the most part Einstein-like in both TlSe and $TlInSe_2$, which may lead to negative Gruneisen parameter for these modes and negative linear expansion coefficient. Note that anti-crossing between acoustic and low-frequency optic branches is similar to that observed in thermoelectric Ba-Ni-Ge clathrates, pointing on both the strong scattering and low velocity of the acoustic waves responsible for heat transport. The last fact, along with giant thermoelectric power [3], puts $TlInSe_2$ in a row with promising thermoelectric materials.

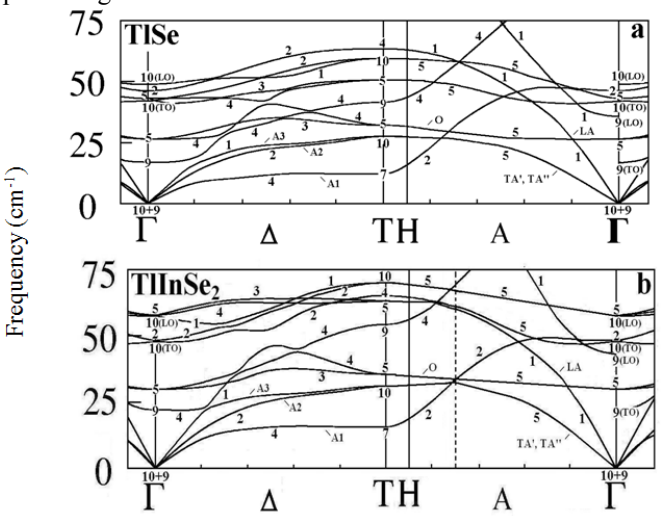

Fig. 2 Low frequency phonon branches along Δ- and A-directions of the Brillouin zone of TlSe (a) and $TlInSe_2$ (b). Vertical broken line shows the wave vector position at which transversal acoustic branch (TA', TA'') and upper phonon branch (O) that has the same A_5 symmetry come too close to each other in $TlInSe_2$..

3. POSSIBLE REASON OF INCOMMENSURATE PHASE TRANSITION

A peculiarity of the phonon band structures of TlSe and $TlInSe_2$ along A-symmetry line is that TA and low frequency optic modes are superimposed, as it is apparent from Fig.2 in which acoustic modes along A-line are indicated as TA', TA'', and LA. Another peculiarity is rather specific and manifests itself in nearly closed-up frequency gap between the transversal acoustic branch (Fig.2, TA', TA'') and upper optic branch (Fig.2, O) at the wave-vector value given by vertical broken line (Fig.1).

Still observable in TlSe (Fig.2a), this gap, however, vanishes upon passing to $TlInSe_2$ (Fig. 2b) and the modes TA and O, having the same A_5-symmetry, tend to touch each other, which is symmetry-forbidden. It is, therefore, natural to assume that there will develop a structural instability that will lead to the phase transition changing the above-situation to the one allowed by symmetry. As a whole, this might be considered as pseudo- Jahn-Teller effect, proposed earlier for driving force of phase transition in $TlGaTe_2$ from nuclear-magnetic-resonance studies [16].

In Fig. 3a the position of the above closing-up on the wave-vector scale is shown by vertical broken arrow and is denoted as I. Exactly the same I-point is found to be peculiar from ARPES of $TlInSe_2$ [6].

Fig. 3b displays the uppermost valence band along A-line of the BZ of $TlInSe_2$ at low temperature (50K) and the excitation photon energy, 11.4eV, necessary to observe the valence band along Γ–H–T direction. The large dots show the experimental data-points at the accessed wave numbers. The full, dotted, and dashed-dotted curves are the results of simulation. (For more details on the simulation results please refer to our work [6].)

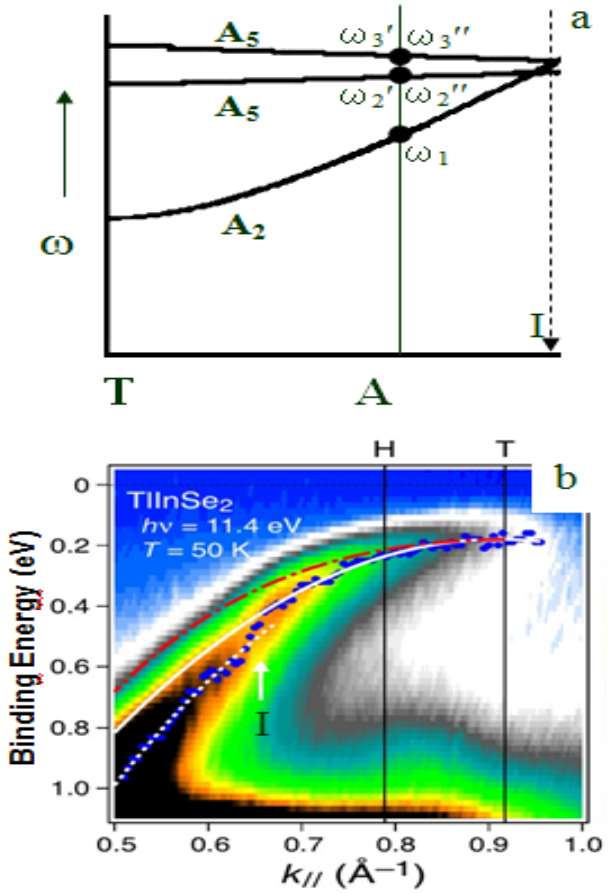

Fig.3 The point (I) related to incommensurate phase transition in $TlInSe_2$: (a) schematic fragment of the phonon band structure of $TlInSe_2$; the cross-points (dots) between the vertical lines and phonon dispersion curves are labelled by ω with subscripted integers increasing with increasing phonon frequency, superscripts ‘ and ‘’ mean that for a given phonon there are two components with the same frequency, vertical broken arrow show the wave-vector position (I) that corresponds to the incommensurate phase; (b) experimental wave-vector dependence of electron binding energy (E) in $TlInSe_2$, as obtained by angle resolved photoemission spectroscopy [6], the gap-like structure at the wave-vector corresponding to the incommensurate phase is indicated by arrow; large dots – experimental points, full, dotted, and dashed –dotted curves – results of simulation .

There is a gap-like structure shown by vertical arrow in Fig.3b, which is impossible for an electronic band of a non-modulated phase and indicates on phase transition in $TlInSe_2$ into modulated phase. Since I-point is an arbitrary point on A-line the phase transition is supposed to occur through intermediate incommensurate phase.

Following our reasoning regarding the nature of the I-point peculiarities, evident from both phonon and electron spectra of $TlInSe_2$, we shall conclude that a possible reason of the incommensurate phase transitions in $TlInSe_2$ might be lattice instability that develops in I-point ($0.67Å^{-1}$[6]) of the BZ with temperature and generates the observed phase transition. If this is true, examination of the valence band of TlSe should bring the evidence that the phase transition (if any) and its manifestation in the form of kink- or gap-like structure are less pronounceable for this material since the closed-up gap between the already-specified phonons slightly opens upon passing from $TlInSe_2$ to TSe (compare Fig2a and Fig. 2b). Otherwise, one shall consider the observed phase transition is related to purely electron subsystem.

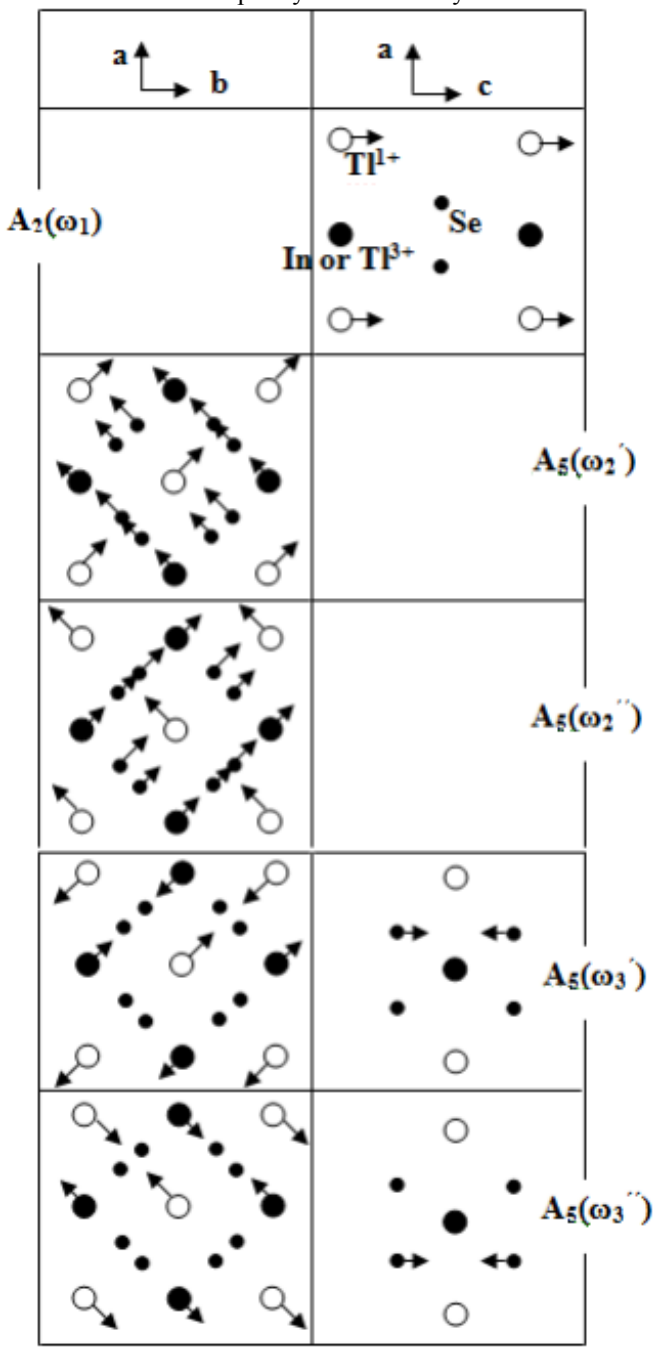

Fig. 4 Atomic displacements in a-b and a-c planes (a,b,c- unit cell vectors) for the phonons along A direction of the Brillouin zone of $TlInSe_2$; the frequency notation of each phonon is given in brackets after phonon’s symmetry, all notations are the same as in Fig. 3.

4. ATOMIC DISPLACEMENTS NEAR I-POINT OF BRULLOUIN ZONE

In Fig.3a in the proximity of the closed-up gap in I-point we have selected a set of the phonon frequencies given by dots and denoted as ω_i (i=1,2,…). The frequencies of the two-fold degenerated modes are denoted as ω_i’ and ω_i’’. The atomic displacements corresponding to the selected set are shown in Fig.4. Only univalent Tl^I atoms are moving along c-direction to form the low frequency A_2 mode with ω_1 frequency. Displacements of all atoms in a-b plane lead to the

phonon with A_5 symmetry, two fold degenerated (ω_2' and ω_2'') in a-b plane. Finally, anti-phase displacements of Tl and In (or threevalent Tl^{III} atoms) in a-b plane, accompanied by anti-phase displacements of Se along c-direction form the optic phonon, O which also have A_5 symmetry and is two-fold degenerated in a-b plane. We would like to mention that the above-picture of atomic displacements is changing while moving along T-H-Γ or T- Γ trajectory. Pure acoustic-type atomic displacements in the neighborhood of Γ point are no longer remaining acoustic away from this point, as it is seen for phonons with ω_2 frequency (Fig. 4).

5. CONCLUSIONS

We have assigned the proper symmetries to all phonons of TlSe and $TlInSe_2$. We have shown that the crossover observed in $TlInSe_2$ between low frequency modes with the same symmetry occurs just in the BZ -point that was earlier identified in ARPES studies in relation to incommensurate phase transition. We have proposed that the driving force of this transition in centre-symmetric $TlInSe_2$ might be pseudo-Jahn-Teller effect. Symmetry considerations related to phase transition are under way.

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