

Phase transitions and Raman scattering spectra of TlGaSe_2

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Abstract. In this work we examined the phase transitions in the ternary thallium chalcogenide TlGaSe_2 by studying the temperature dependence of the Raman spectra with the aid of confocal microscopy. The unpolarized Raman scattering spectra of TlGaSe_2 single crystals were measured over the temperature range 78–300 K (which includes the range of the successive phase transitions) in the frequency region of 50 – 300 cm^{-1} . The Raman spectra exhibited 12 lines at 300 K, but the number of lines rose to 17 at 78 K. In the temperature interval between 107 K and 120 K, where the phase transitions take place, the temperature dependence of the phonon frequencies showed discontinuities for several of the Raman lines.

1. Introduction

Ternary thallium chalcogenides with chemical formula TlMeX_2 (where Me = In, Ga and X = Se, S, Te) belong to a family of semiconductors with a chain or layered structure. These compounds exhibit phase transitions at low temperature. Detailed information about the phase transitions and other properties of these compounds has been collected in a topical review by Panich [1]. In one way or another, the properties are related to successive phase transitions, the nature of which is not yet completely understood.

Many previous studies of TlGaSe_2 which belongs to TlMeX_2 family have been reported [2-5]. It is commonly accepted that the temperature-dependent structural changes in TlGaSe_2 are manifestations of a phase transition from a normal (N) to a commensurate (C) state via an intermediate incommensurate (I) phase. For these phase transitions Ti (N-I transition) and Tc (I-C transition) are around 107 K and 120 K, respectively. As a result of this transition, the unit cell in the ferroelectric C-phase is quadrupled in the crystallographic direction c. However, a manifestation of this quadrupling in the Raman spectra of TlGaSe_2 has not been observed.

Although the Raman spectra of TlGaSe_2 have been studied comprehensively, the details of the line shapes and their temperature dependence are poorly understood. We decided to study the phase transition in TlGaSe_2 by measuring the temperature dependence of the Raman spectra using a confocal spectroscopy system.



2. Experimental details

Single crystals of layered TiGaSe_2 were grown by the Bridgman-Stockbarger method. The unpolarized Raman spectra were recorded in the frequency range $50\text{--}300\text{ cm}^{-1}$ in a backscattering geometry such that the electrical field vectors of the incident and scattered light were nearly perpendicular to the normal to the layer plane and c -axis. The sample was mounted in a special vibration-free cryostat and its temperature was varied between $78\text{--}300\text{ K}$. (This includes the temperature range where the series of phase transitions is believed to occur.) A 532 nm diode-pumped solid-state (DPSS) laser was used as the light source. The spectral resolution was better than $\pm 0.8\text{ cm}^{-1}$.

3. Results and discussion

The Raman spectra of a TiGaSe_2 crystal at 78 and 300 K are shown in Figure 1. In the frequency region of $50\text{--}300\text{ cm}^{-1}$ the spectra exhibit at least 12 Raman modes at 300 K and the number rises to 17 at 80 K . Table 1 summarizes the numerical values of the modes frequencies shown in Figure 1. This table also includes Raman peaks reported by other researches [2 - 4] in the frequency range of $50\text{--}300\text{ cm}^{-1}$.

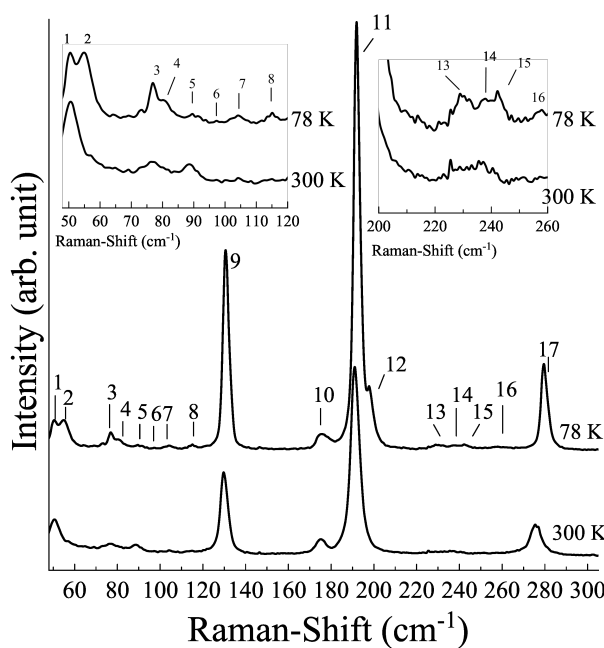


Figure 1. Raman spectra of TiGaSe_2 at 78 K and 300 K . (Numbers correspond to the list in Table 1.)

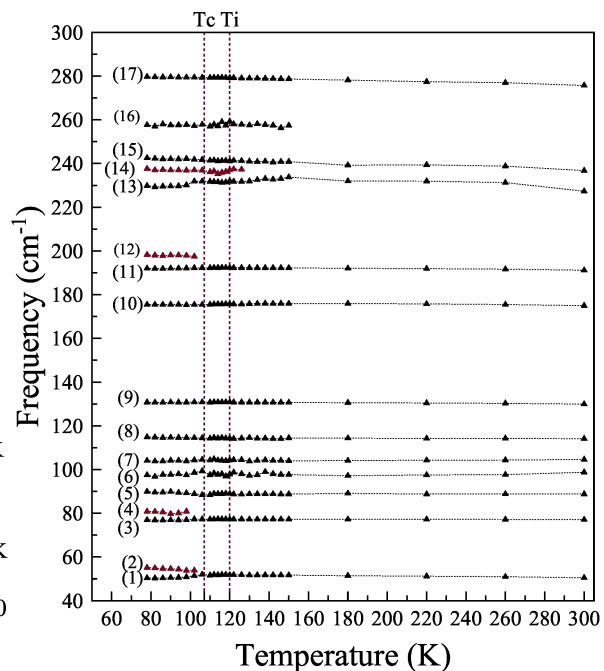


Figure 2. Temperature dependence of the mode frequencies of the Raman spectra of TiGaSe_2 . The dashed lines represent guides for the eyes. (Number correspond to the list in Table 1.)

Each mode in the measurement Raman spectra was deconvoluted into Lorentzian peaks, using a least squares procedure. The temperature dependence of the modes is shown in Figure 2. As the temperature decrease, additional Raman lines suddenly appear at frequencies of about 56 , 82 , 199 and 237 cm^{-1} , this is an indication of a structural phase transition at low temperatures [2]. More detailed information about the temperature dependences of the frequency and width (FWHM) of the lines is given in Figure 3. We can clearly observe that in the temperature interval between $T_c = 107\text{ K}$ and $T_i = 120\text{ K}$, where the phase transition takes place, the temperature dependence of the phonon frequency and the width of the peak show discontinuities for the highest intensity Raman modes (1, 9, 11 and 17). These results partly agree with those reported earlier [5], where pressure dependence of phonon

frequencies in TiGaSe_2 also showed discontinuities for modes 1, 11 and 17. Furthermore, from Figure 3 we can also observe also that the mode width (FWHM) exhibits broadening with the temperature increases. This fact explains why Raman modes are clearly resolved at low temperatures, while some closely spaced modes are not resolved at high temperatures.

Table 1. Raman modes frequencies (ν_i) in TiGaSe_2 at low and room temperature.

Number of the mode	Ref. [2] $\nu_i (\text{cm}^{-1})$		Ref. [3] $\nu_i (\text{cm}^{-1})$	Ref. [4] $\nu_i (\text{cm}^{-1})$	This work $\nu_i (\text{cm}^{-1})$	
	85 K	300 K	300 K	300 K	80 K	300 K
1	53	54	54	53	50.4	50.5
2	56	-	-	-	55.1	-
-	74	-	-	-	-	-
3	79	-	-	-	78.9	77.1
4	83	82	82	80	80.8	-
5	87	88	88	-	89.9	88.8
-	92	-	-	91	-	-
6	-	-	-	-	97.4	98.8
7	106	105	105	105	104.1	104.6
8	118	-	-	-	114.9	114.1
9	133	133	133	132	130.8	129.9
-	-	-	163	-	-	-
10	-	-	-	177	175.5	174.9
11	194	194	194	193	192.0	191.2
12	199	198	198	-	198.2	-
-	204	-	-	-	-	-
13	231	230	230	229	229.8	227.2
14	240	240	240	-	237.6	-
15	244	-	-	-	242.5	236.8
-	250	250	250	249	-	-
16	260	-	-	-	257.6	-
-	-	268	268	-	-	-
17	280	278	278	278	279.7	275.7
-	285	-	-	-	-	-

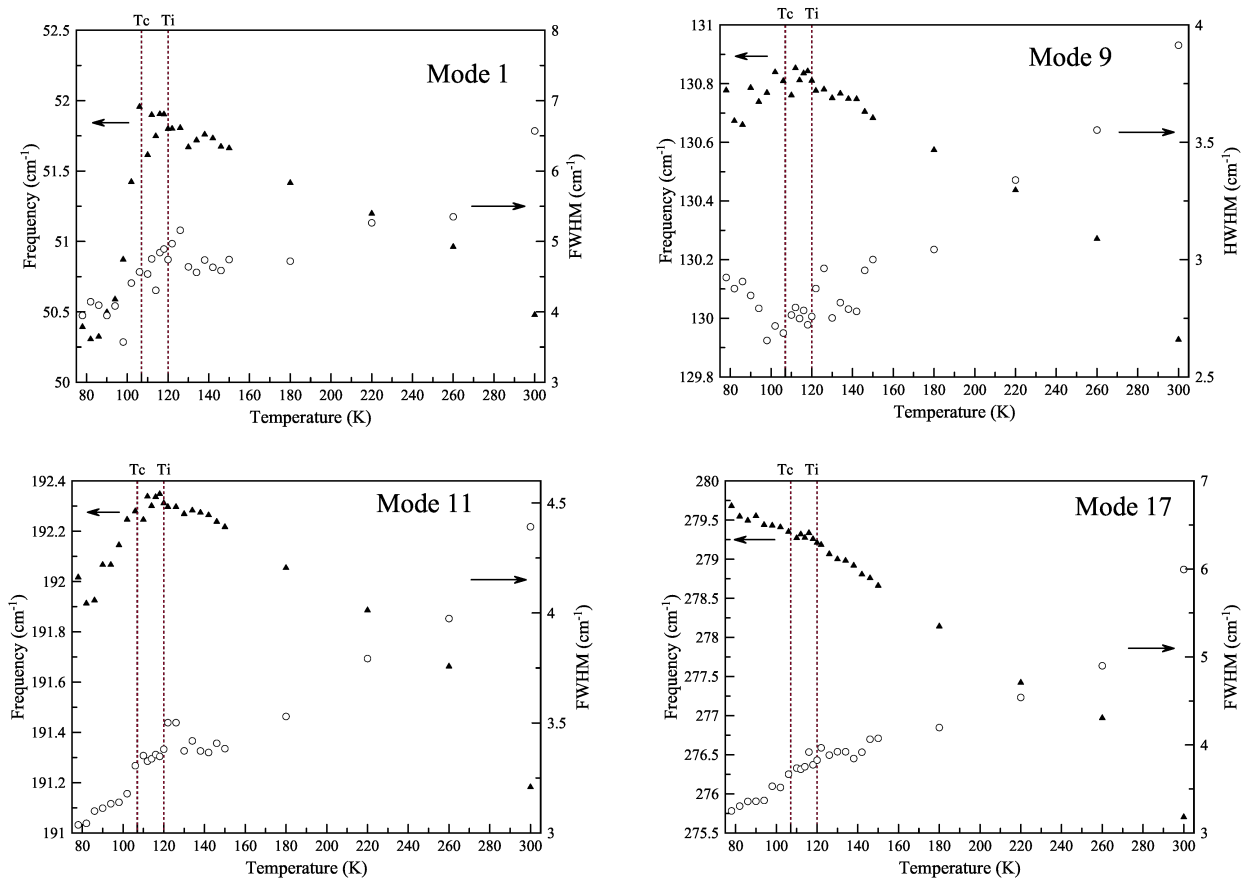


Figure 3. Temperature dependence of frequency and width (FWHM) of Raman modes. (Numbers correspond to the list in Table 1.)

4. Conclusions

We have studied the temperature dependence of the frequency and peak-width of the Raman lines in TiGaSe_2 including the temperature range of the reported ferroelectric phase transition through an intermediate incommensurate phase. Our results indicate a complicated picture that cannot be fully explained within the theoretical framework of phase transitions previously reported for TiGaSe_2 . More studies of the broadening and peak position as a function of the temperature are necessary to fully understand the results obtained in this study. A re-examination of the Raman scattering spectra over a wider range of frequencies and temperatures as well as polarized Raman measurements are under way.

Acknowledgements

This work was supported in part by Japan Ministry of Education, Culture, Sport, Science and Technology under the grant-in-aid No 23560371.

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