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Low-Temperature Phase Transition in Tl In Se_2 Crystals

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Abstract

Heat capacity, lattice parameter, spectral and temperature dependences of photoconductivity of chained crystal Tl In Se_2 have been investigated in this work. For the first time, it has been found that the phase transtion takes plase at temperatures 135 and 184 K in this crystal. The changes of heat capacity, photoconductivity and lattice parameter of Tl In Se_2 in the region of phase transition is supposed to be connected with the presence of an incommensurate phase in this crystal.

1. Introduction

$TlInSe_2$ as well as $TLGaTe_2$ and $TLInTe_2$ crystals have a layer-chained structure, tetragonal syngoniya of spatial group symmetry 14/mcm-D_{4h}^{18} and are ternary analogue of TlSe crystal [1]. In the structure of $TlInSe_2$, trivalent atoms of indium are connected with four atoms of selenium through covalence binding. These $In^{3+}Se_4^{2-}$ tetrahedrons form the chains stretched along the "C" axis. The single-valence atoms of thallium are connected with the chains of the tetrahedrons by ionic binding. Thus the structure of this compound can be represented by two subsystems: the rigid subsystem of negatively charged chains ($InSe_2$) along the "C" axis, and the more mobile system of thallium atoms. This paper presents results of an investigation of the temperature dependence of lattice parameters, heat capacity and photoconductivity of Tl In Se_2 crystals in the 80- 300K temperature range. The interest of such kind of investigations is caused by following circumstances. Firstly, it was predicted theoretically [2] that phase transition is possible in TlSe type crystals, to which $TlInSe_2$ belongs. Secondly, an incommensurate phase transition was found to exist in isostructural $TlGaTe_2$ crystals [3]. Moreover, the structural phase transtion had also been revealed via Raman scattering spectroscopy, neutron scattering, capacitance and calorimetry methods in other $A^{III}B^{III}C_2^{VI}$ ternary crystals such as Tl Ga Se_2 and Tl In S_2 [4-7].

2. Experimental Methods

X-ray investigation has been carried out using X-ray diffractometer DRON-3 (Cu, Kα -radiation) with low temperature attachement URNT-180, which allows to carry out X-ray mesurements at low and high temperatures. Heat capacity temperature dependence C_p(T) was mesured using an adiabatic calorimetry installation with automatic control of temperature, in steps of 0.5 K. $TlInSe_2$ samples photoconductivity was mesured by synchronous detection method with flux intensity modulated light in the (20- 1200) Hz frequency interval using a MDR-23 monochromator in the spectral region 450-1014 nm. The external electric field **E** was applied along the direction of crystal chains (**C**) through indium contacts plated on high quality natural surfaces of the samples. The photoconductivity mesurements were carried out in the small-load resistance regime ($R_{Ioad} \ll R_{sample}$), when the photosignal ΔU is proportional to the change of sample's static conductivity $\Delta\sigma \cdot \Delta\sigma(\lambda)$ spectral dependence was registered for two electromagnetic radiation polarizations $\mathbf{E} \parallel \mathbf{C}$ and $\mathbf{E} \perp \mathbf{C}$.

3. Results and Discussion

From detailed X-ray investigation of Tl In Se_2 it was discovered the unusual temperature behaviour of the "a(T)" lattice parameter. As it is shown in Figure 1b, the lattice parameter "a(T)" is almost constant within the temperature regions 130-140, 170-185 and 200-220K. However, "a(T)" increases monotonically with temperature outside of these regions. The lattice parameter "c" also shows the anomalies at the same temperature regions. Bragg reflexes correlates well with temperature dependence of "a". It should be noticed that the presence of plateau regions in the lattice parameters temperature dependence is characteristic for the phase transition phenomenon which has been observed in such compounds as ZnP_2 [9], CdP_2 [10], $RbZnO_3$ [11], $Sr_2Nb_2O_3$ [12] and others. It must be emphasized that for all crystals mentioned above the invariable sections in the temperature dependence of the lattice parameter "a(T)" correspond to incommensurate phase.

Due to anomalies observed in the lattice parameters temperature dependence we have carried out more detailed investigationso f C_p(T) in monocrystalline $TlInSe_2$. It must be noticed that temperature dependence of C_p(T) in polycrystalline $TlInSe_2$ does not have a phase transition anomaly [8]. But the numerical values of C_p in the investigated region were in good agreement with that presented in paper [8].

Ten different series of C_p(T) mesurements have been carried out and one of the results is presented in Figue 1a. As seen in this figure, there are two anomalies in "C_p(T)": in the temperature regions 130-140K and 180-188K. At these temperatures gn $TlInSe_2$ crystal there are changes of C_p(T) is weak. In the phase transition region $\Delta C_2 = (5.21 \pm 0.05)$ J/(mol K) at T=184K for the mesurement presented in Figure 1a. The value of ΔC_p and the temperature at which the anomaly takes place changed at repeatedly among mesurements and thus depend on the rate of heating. It should be noticed that for $TlGaTe_2$, $TlGaSe_2$ and $TlInS_2$, which also belong to $A^{III}B^{III}C_2^{VI}$ ternary crystals, commensurate-incommensurate character of phase transition was established. It is also notable that hysteresis of the mesured parameters was typical of such crystals.

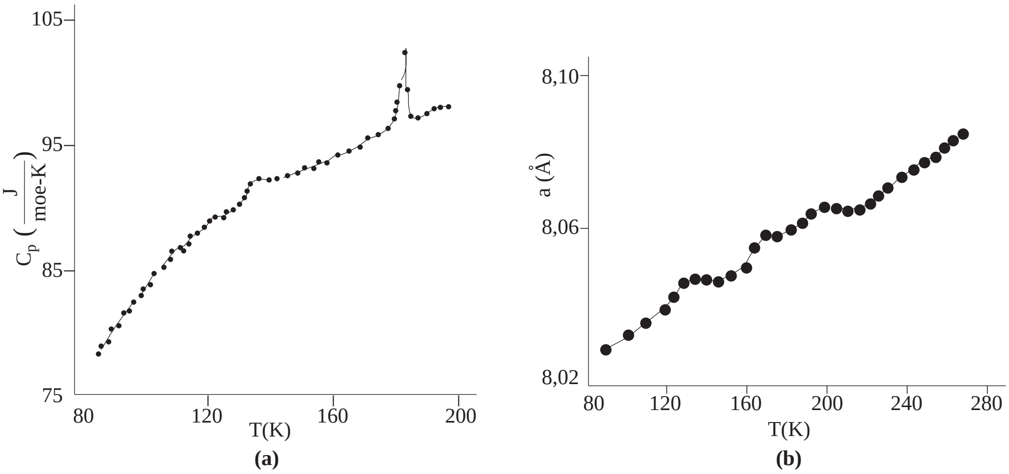

Figure 1. a) Temperature dependence of heat capacity of $TlInSe_2$; b) Temperature dependence of lattice parameter "a(T)".

Figure 2 shows an example the most frequently obtained photoconductivity spectra, normalized by equal number of quanta of incident radiation at T=300K and T=80K of $TlInSe_2$ monocrystals for two polarizations of light. At T=300K and $\mathbf{E}\|\mathbf{C}$ the photoconductivity spectrum possesses maxima at ε=1.45eV, ε=1.85eV and ε=2.46eV. For $\mathbf{E}\perp\mathbf{C}$, the photoconductivity maxima are shifted to lower energies by approximatly $\Delta\varepsilon$=0.1eV. For both polarizations the T=300K photoconductivity spectra have a minimum at $\varepsilon \approx$ 1.5eV for all samples investigated in this work. As seen from Figure 2, at T=300K the intensities of short wave maxima, which correspond to deeper interband transitions, exceed the intensities of band edge transitions for both polarizations.

Thus the high temperature photoconductivity spectra indicate the presence of two edges of $TlInSe_2$ for two mutually perpendicular polarizations of light ($\mathbf{E}\|\mathbf{C}$ and $\mathbf{E}\perp\mathbf{C}$). In some samples (which are reraly founded) the high energetic PC maxima for $\mathbf{E}\|\mathbf{C}$ are situated at ε=1.79eV and ε=2.25eV with corresponding pairs for $\mathbf{E}\perp\mathbf{C}$ at ε=1.65eV and ε=1.92eV. We have analyzed a complex of photoconductivity spectra obtained at T=300K for both $\mathbf{E}\|\mathbf{C}$ and $\mathbf{E}\perp\mathbf{C}$ polarizations for a greet number of $TllnSe_2$ samples. The results show the presence of peculiarities due to interband optical transitions at the following values of the quantum energies:1.45eV, 1.5eV (as a minimum of photoconductivity), 1.79eV, 1.85ev, 2.25eV, 2.46eV for $\mathbf{E}\|\mathbf{C}$ and of 1.35eV, 1.5eV (as a minimum of photoconductivity), 1.65eV, 1.72eV, 1.92eV for $\mathbf{E}\perp\mathbf{C}$. The photoconductivity spectra at T=80K (curves 3 and 4) exhibit essential differences for the high temperature cases. The main difference is the absence of polarizing dependence of intensity and position of photoconductivity maximum corresponding to the band edge transition situated at ε=1.26eV. In addition, the values of photosignal ΔU at low temperatures are much smaller than those of at T=300K. The differences at the edge indicate the degeneration of electron states in this point at low temperature caused by the change of crystal symmetry. Figure 3 shows the temperature dependence of photosignal ΔU(T) when the sample was illuminated by monochromatic light with fixed quantum energy ε=2.5eV in the heating regime. Dependecies such as this were obtained for all quantum energies greater than the high temperature forbidden gap. Note that ΔU(T) dependence also has a hysteresis which depends not only on heating and cooling regimes but on intensity of light and (weakly) on quantum energy also. It is seen that the drastic change of photosignal ΔU takes place beginning at T=135K and T=185K. The photosignal in the temperature range (140-170 K) is 10^4 times lower than that at T=300K. This fact complicates the investigation of temperature dependence of the photoconductivity edge. It is difficult, in particular, to answer the question of what is the reason for the shift of the edge to the lower energies at low temperature?

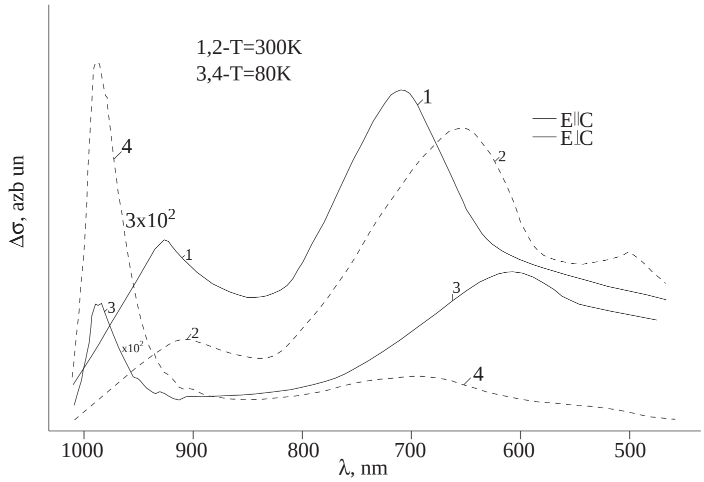

Figure 2. Spectra dependence of photoconductivity of $TlInSe_2$ for "**E**$\|$**C**" and "**E**$\perp$**C**" at T=80K and T=300K.

Is $(\partial_{\varepsilon_g}/\partial T) > 0$ in this crystal in sufficiently large temperature interval? Or is this due to the commensurate -incommensurate- commensurate phase transition, and as a consequence of the band structure and forbidden gap change. We think that the increase of $\Delta\sigma$ (about 40-50 %) over the narrow temperature range 125-130K is apparently due to the increase of dielectiric constant when the temperature approaches the phase transition point, and, as a consequence, the mobility of photoexcited carriers increase. Because at low temperatures the main scattering mechanism for carriers is scattering by ionized impurity center. Note that our attempt to investigate the phase transition with capacitance method by mesuring the real part of the dielectric constant of $TlInSe_2$ was failed because of the relatively high conductivity ($\sigma \sim 10^{-2}$ ohm$^{-1}\cdot$cm^{-1}) of the samples. A fast decrease of the photoconductivity in the temperature range (135-175 K) is related to the transition into the incommensurate phase where the concentration of the capture and scattering centers are considerably more than those in the low-symmetric and high symmetric phases. It must be noticed that similar PC dependence on temperature had been obtained in [12] where an attempt was made to explain it by the presence of two types of r-centers in samples. In the inset of figure 3 the dependence of the photoconductivity on radiation intensity modulation frequency is shown at T=300K, T=80K and in the temperature range (140-170K). These data show that the lifetime in the incommensurate phase is much less than that in the commensurate phase. An abrupt increase of $\Delta\sigma$ at T> 180K is connected with a transition from the incommensurate to the commensurate phase and as a consequence of the increase of lifetime and mobility of the photoexcited carriers owing to decrease of consentration of the scattering centers.

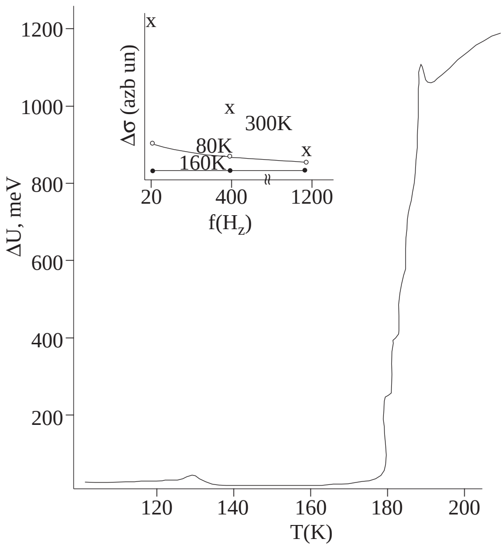

Figure 3. Temperature dependence of photoconductivity at =2.5eV. Inset shows the modulation frequency dependence of photoconductivity at different temperatures.

3. Conclusion

Investigation of the temperature dependence of heat capacity, lattice parameters and photoconductivity spectra of $TlInSe_2$ monocrystals show that there is a phase transition connected with forming of the incommensurate phase in the temperature interval between 135K and 185K.

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