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DSC and EPR investigations of structural phase transitions in thallium indium disulphide single crystals

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The results of Differential Scanning Calorimetry (DSC) and Electron Paramagnetic Resonance (EPR) investigations of $TlInS_2$ single crystal in the temperature range of structural phase transitions are presented. The temperature dependence of the heat capacity $C_p(T)$ has been obtained using DSC as a new technique applied to this crystal and relevant anomalies of $C_p(T)$ at the temperatures of the phase transitions have been revealed. These anomalies are in accordance with obtained significant changes in EPR spectra, associated with strong splitting existing resonance lines and appearance of additional lines at the temperatures of the phase transitions below 200 K. The results are discussed in comparison with earlier reported data on structural transformations in $TlInS_2$.

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1. Introduction

$TlInS_2$ is a ternary chalcogenide crystal, which belongs to the group of semiconductors having layered crystalline structure. It crystallizes in monoclinic system and belongs to a space symmetry group of C_{2h}^6 at room temperature [1, 2]. The presence of ferroelectric phase transitions in $TlInS_2$ was firstly reported from dielectric constant measurements [3]. Later it has been established that $TlInS_2$ exhibits a sequence of structural phase transitions to incommensurate (IC) and commensurate (C) phases. According to neutron [4] and X-ray scattering investigations [5], the transition to IC phase occurs at about 216 K and is associated with condensation of a soft mode at the point in the Brillouin zone with q_i (δ, δ, 0.25), where δ is the incommensuration parameter (δ = 0.012). On subsequent cooling, $TlInS_2$ exhibits IC-C phase transition at the temperature of T_{c1} ~ 200 K with condensation of the soft mode at q_c = (0, 0, 0.25), which accompanied by the quadrupling of the unit cell volume along the direction perpendicular to the layers. However, the presence of the ferroelectric soft mode with Curie temperature at about T_c ~ 200 K and with the Curie constant ~ 10^3 was discovered by submillimeter spectra and dielectric constant measurements [6]. It was revealed that the spontaneous polarization vector of the ferroelectric phase lies in the plane of layers.

Heat capacity is one of the basic pure component material properties and its knowledge has particular importance for many scientific and engineering calculations [7]. Specific heat investigations in such crystals having a complex structure and obviously expressed chemical bond anisotropy are of interest to elucidate unique features of thermal oscillation dynamics in complex layered semiconductors [8]. DSC has been used for over forty years to characterize many thermal properties in materials. Being a thermal analysis technique, DSC detects the temperatures and heat flows caused by changes in heat capacity or by endothermic and exothermic processes of materials as a function of time and temperature [9].

There are some works in literature, where the results of the investigations of the heat capacity of $TlInS_2$ crystal were reported [10-12]. The present work reports the results of the study of the heat capacity of $TlInS_2$ single crystal using DSC technique, which is applied to this compound for the first time. Additionally, EPR is also used as an additional technique in order to analyze the heat capacity anomalies, which are interpreted as the results of the structural transformations. In addition to this main aim, this study intends to reveal the applicability of DSC on the thermal measurements depending on the heat capacity comparisons with the data of relevant compounds existing in literature.

2. Experimental

$TlInS_2$ single crystals were synthesized from high-purity elements (at least 99.999 % pure) held in stoichiometric proportions using modified Bridgman method. The quality of the samples and the orientation of the crystal planes were controlled by X-ray diffraction measurements. The crystals were suitable to be cleaved into the plane parallel-plates along the (001) basal plane, which is perpendicular to the c-axis. The morphology of the crystal allowed performing this operation.

DSC measurements were carried out in DSC 2010 equipment from TA Company instruments. DSC 2010 is advanced equipment providing a fundamentally more accurate way of measuring heat flow. DSC detects enthalpy changes (heat flow difference) as distinct from Thermomechanical Analysis (TMA) detecting kinetic properties, Differential Thermal Analysis (DTA) detecting temperature (temperature difference), and Thermogravimerty (TG) detecting Mass (mass change). The heat sink was cooled with liquid nitrogen. The level of liquid nitrogen was kept constant during the DSC measurements. In order to purge the system, helium gas was constantly passed through the heat sink and over the cells. After calibration for temperatures and calorimetric sensitivity of the DSC equipment, the optimum heating rate was determined to be 10 K/min through the entire temperature range. The mass of $TlInS_2$ was taken 14.5 mg. Measurements on the sample was carried out in the temperature range of 140 to 280 K.

For EPR measurements Fe^{3+} ions were added to the growth mixture in amounts corresponding to a molar ratio Fe/In of about 0.7 %. The EPR spectra were recorded by using Bruker EMX model X-band spectrometer (9.5 GHz). The static magnetic field was varied in the range 0-16000 G. The field derivative of microwave power absorption (dW/dH_1) was registered as a function of the applied magnetic field H_1. The static magnetic field (H) direction was oriented along (100) plane (paralel to the layers). The temperature dependence of EPR spectra was studied in the range of 20-300 K using continuous helium gas flow cryostat made by *Oxford Instruments* with the temperature stability better than 0.5 K.

3. Results and discussion

The temperature dependence of the heat flow in $TlInS_2$ obtained in a result of DSC measurements is shown in Fig. 1. As it is obviously seen from the figure, two endothermic processes take place in the temperature range between 150 and 300 K with specific peaks at 258.60 and 266.26 K.

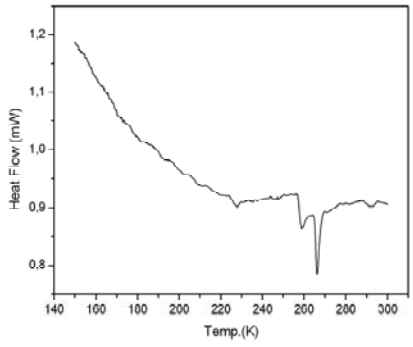

Fig. 1. Temperature dependence of the heat flow in $TlInS_2$ obtained from DSC measurement.

The temperature dependence of specific heat capacity ($C_p(T)$) of $TlInS_2$ in the temperature range of 140-280 K, which was obtained from heat flow curve, is presented in Fig. 2. We have extrapolated our C_p values on both sides with using the C_p data given in [11] in order to see the ordinary heat capacity curve progression, as shown in the figure. As it is seen from the figure, several C_p anomalies were obtained at T = 163.6, 184.9, 193.4, 201.4, 212.6, 236.9, 254.4, and 259.7 K in the temperature range between 150 and 300 K. The anomalies at $T_1 = 163.6$ $T_2 = 184.9$, $T_3 = 212.6$ and $T_4 = 254.4$ K are more intense and their discontinuity amounted to approximately 10%, while the other anomalies appear as small deviations by 4-5% from the regular values which denote the values of the normal curve progression. Some of these anomalies coincide with temperatures of structural phase transitions previously reported in literature.

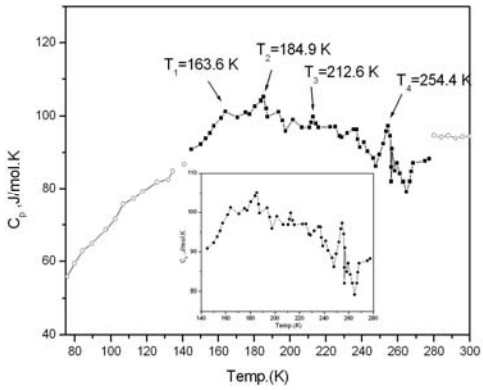

Fig. 2. Temperature dependence of the specific heat of $TlInS_2$ single crystal, ○ indicates the values taken from [4] to extrapolate C_p curve in the range 80-300 K. C_p values determined using DSC are represented by.

On the base of DSC investigations, the calorimetric enthalpy change of the sample is evaluated as 562.05 J/mol by integrating of the C_p curve after subtracting the baseline, which was determined according to the normal heat capacity behavior. The entropy change has been also determined and evaluated as 3.75 J/mol.K by dividing ΔC_p by temperature.

Comparing the presented DSC results with the information on the heat capacity measurements in $TlInS_2$ reported earlier in the literature, one must mention one of the published data [11], which was obtained for a powder sample using of adiabatic calorimetry technique in the range of 5-300 K. The authors reported that anomalies in $C_p(T)$ were obtained at the temperatures of 173.4, 196.9, 206.1, 208, 210.9 and 214.9 K. These results were interpreted on the base of existing of a sequence of phase transitions associated by coexistence of long-period commensurate and incommensurate phases. On the other hand, the results of heat capacity measurements performed using the thermal relaxation method in the temperature range of 60-310 K, were presented in [12]. The authors reported anomalies in $C_p(T)$ of $TlInS_2$ at the temperatures 156, 166, 173, 192, 202, 207, 216, 222, 227.5, 244, 253, and 258.5 K. It is noted that our anomaly values are in accordance with these temperatures differing by amount of 1-3 K. Actually, all $C_p(T)$ anomalies determined from DSC measurements appear inside the phase transition temperature interval observed elsewhere

[13, 14]. Additionally, we should point out that, even though there was a fluctuation-type anomaly of C_p near the temperature of IC phase transition and obvious maximum at C phase transition temperature, it is not possible to interpret all $C_p(T)$ anomalies on the base of existing theories regarding the successive phase transitions from a symmetric to IC and C phases [15, 16].

Generally, as many other macroscopical measurements, heat capacity measurements are insufficient to completely describe and interpret structural phase transitions. It is well known that the EPR is a well-established method of the investigation for many problems in condensed matter, including structural transformations. EPR experiments utilize paramagnetic probes incorporated into crystal lattice to obtain information about local structural changes in their surroundings. The results of our investigations of the temperature dependence of EPR spectra of $TlInS_2$ compound doped by paramagnetic Fe^{3+} ions are reported in our previous works [17, 18]. Here we report additional information regarding new EPR experiments on $TlInS_2$ especially in the frame of consideration of DSC results reported above.

As it was mentioned in [17, 18], the observed EPR spectra of iron doped $TlInS_2$ can be interpreted to correspond to the transitions among the spin multiplets (S = 5/2, L = 0) of the Fe^{3+} ions substituted for the In^{3+} sites at the central positions of InS_4 tetrahedrons in $TlInS_2$ crystal lattice. This substitution requires no charge compensation but the ionic radii of the two ions are quite different (0.080 nm for In^{3+} and 0.063 nm for Fe^{3+}). EPR spectra of Fe^{3+} doped $TlInS_2$ crystals at various temperatures between 10 K and 300 K on applying the static magnetic field in the direction perpendicular to the plane of crystal layers (out-of-plane geometry) are presented in Fig 3.

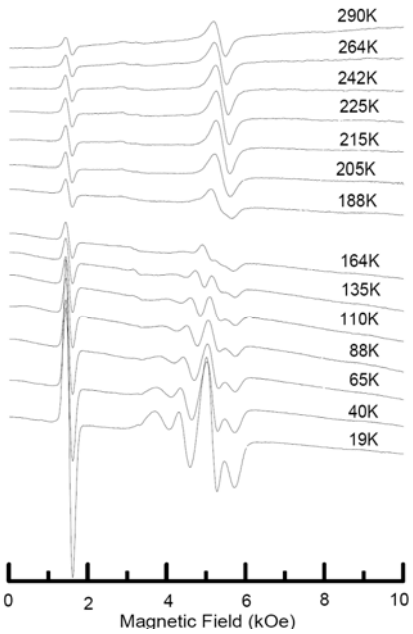

Fig. 3. EPR spectra of Fe^{3+} doped $TlInS_2$ at different temperatures.

The temperatures in the figure are selected in accordance with the significant temperature changes of EPR spectra. It can be seen clearly that, the EPR spectra depend significantly on temperature in a wide temperature range. The spectra exhibit considerable changes at the temperatures below 200 K. As it is seen from the figure, two resonance lines are seen on EPR spectra observed at 290 K at ca. 1505 Oe (1) and 5303 Oe (2). Though just a little shift of 30 Oe and a drastic increase in the amplitude is observed for the first line on lowering the temperature, the second line exhibits both splitting and multiplication of resonance lines. At 19 K this line splitted to four different lines at ca. 3872, 4446, 5174, and 5590 Oe. The rotation patterns of all these resonance lines were presented and discussed in our previous studies [17, 18] and best fitted EPR parameters were obtained as g= 2.00, D=0.7350 (0.7800) cm^{1-} and E= 0.1700 (0.1645) cm^{1-} for two different types of centers in $TlInS_2$ crystal lattice at low temperatures.

The temperature dependences of the resonance field values observed in out-of-plane geometry in the temperature interval between 25 K and 300 K are shown in Fig. 4. These dependences obviously show the processes of splitting and multiplication of the resonance lines on lowering the temperature and passing through the temperature points where we obtained the heat capacity anomalies by DSC. While the resonance line at 1520 Oe indicates obviously no temperature dependence on heating the crystal, the other four resonance fields $H_{res}(1)$ = 3870 Oe, $H_{res}(2)$ = 4420 Oe, $H_{res}(3)$ = 5150 Oe, and $H_{res}(3)$ = 5590 Oe show strong temperature dependences and, at around 210 K, transformed to a single field line at 5410 Oe.

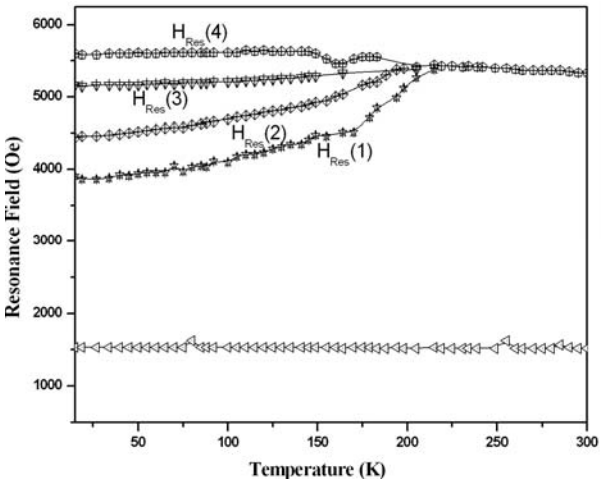

Fig. 4. Temperature dependences of the positions of the observed resonance lines of EPR spectra of Fe^{3+} doped $TlInS_2$.

Thus, as it is obviously seen from the results of EPR investigations, the structural phase transformations in $TlInS_2$ crystal take place only in the temperature interval near 200 K. On the other hand, the temperature dependence of the heat capacity exhibited a number of

anomalies in a wider temperature range with little differences from the other published data about $C_p(T)$ anomalies. These differences can result from a couple of reasons; e.g. the quality of the crystal and growth conditions. It should be mentioned that the modulation dependence on temperature in the range of 190-220 K, where three maxima take place, can be explained on the basis of assumptions of existing partial devil's ladders (long-periodic commensurable phases) inside of the temperature interval of incommensurate phase [13, 14].

4. Conclusions

Thus, considerable changes of Electron Paramagnetic Resonance spectra of Fe^{3+} ion have been observed at the temperatures lower than 200 K, which was attributed to a strong splitting and appearance of multiplication. This behavior of resonance lines reflects the temperature induced changes in the crystal structure due to the occurrence of structural phase transitions in the temperature ranges as evidenced in many cases [19-21] and, as a result, confirms the detected heat capacity anomalies as structural phase transitions in the same temperature interval. Additionally, in the light of all these obtained results and comparisons with published data, it can be stated that Differential Scanning Clorimetry has a particular potential in the field of thermal measurements of crystals.

Acknowledgments

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