LOW TEMPERATURE ELECTRON PARAMAGNETIC RESONANCE INVESTIGATIONS OF Fe^{3+} DOPED FERROELECTRIC $TlGaSe_2$ CRYSTAL

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Işdə 15-300K temperatur intervalında Fe^{3+} aşqarlanmış $TlGaSe_2$ monokristallarının EPR metodu ilə tədqiqinin nəticələri göstərilmişdir. 110K–dən aşağı temperaturlarda EPR spektrlərində rezonans xətlərinin parçalanması və əlavə xətlərin yaranması müşahidə olunmuşdur. EPR spektrində müşahidə olunan bu dəyişiklik struktur faza keçidləri zamanı Tl ionlarının yerdəyişməsi və nizamlanması ilə əlaqədardır.

В работе представлены результаты исследований методом ЭПР легированных Fe^{3+} монокристаллов $TlGaSe_2$ в температурном диапазоне 15-300 K. Существенные изменения спектров ЭПР, заключающиеся в сильном расщеплении и появлении дополнительных резонансных линий, наблюдались при температурах ниже 110 K. Наблюдаемые изменения в спектре ЭПР связаны со смещением и упорядочиванием ионов Tl при структурных фазовых переходах.

This paper presents the results of EPR investigations of Fe^{3+} doped $TlGaSe_2$ single crystals in the temperature range of 15-300 K. Some certain significant changes of EPR spectra, which are associated with a strong splitting and appearance of additional resonance lines, were observed at the temperatures below 110 K. Such transformations are considered as result of displacements and ordering of Tl ions during the structural phase transitions

INTRODUCTION

$TlGaSe_2$ is a ternary-layered chalcogenide crystal, which crystallizes in monoclinic system and belongs to a space symmetry group of C_{2h}^6 at room temperature [1]. According to X-ray diffraction measurements [2,3], the crystal structure of $TlGaSe_2$ is characterized by metal-chalcogen layers composed of Ga_4Se_{10} polyhedron complexes representing a combination of four elementary $GaSe_4$ tetrahedra linked by common chalcogene atoms at the corners. The elementary unit cell contains two layers, containing successive rows of the tetrahedron complexes, which are turned away from each other by 90^0 and each of them is shifted by the length of the edge of the small $GaSe_4$ tetrahedron with respect to another layer along $[1,1,0]$ and $[1,\bar{1},0]$ directions. Monovalent Tl atoms are located in trigonal prismatic cavities between metal-chalcogen layers. As a result, a deviation from the tetragonal symmetry appears. The angle between the monoclinic c axis and the layer plane is about 100^0.

As it is mentioned in [4], the origin of the disorder in the crystal structure of $TlGaSe_2$ is due to the fact that owing to the stacking variants and the pseudo tetragonal symmetry, the crystal frequently contains four layer type twins, where the monoclinic axis are exchanged or the tilting is in the opposite direction.

The first publication about the presence of structural phase transitions and ferroelectricity in ternary-layered chalcogenide crystal $TlGaSe_2$ was published about two decades ago [5]. Many researchers investigated the promising structural phase transitions of this compound by using a great number of experimental methods since that time. It has been concluded that, on cooling, $TlGaSe_2$ exhibits a sequence of structural phase transitions, including transitions to an incommensurate (IC) and commensurate (C) phases. According to neutron [6] and X-ray scattering investigations [3], the transition to IC phase, which takes place at T_{i1}~120 K, is associated with condensation of a soft mode at a point in the Brillouin zone characterized by $\mathbf{q_i}(\delta,\delta,0.25)$, where δ is the incommensuration parameter (δ= 0.02). On subsequent cooling, $TlGaSe_2$ exhibits IC-C phase transition at the temperature of T_{c1}~ 107 K with condensation of the soft mode at $\mathbf{q_c}$=(0,0,0.25), which accompanied by the quadrupling of the unit cell volume along the direction of perpendicular to the layers. However, the presence of the ferroelectric soft mode with Curie temperature at about T_c~107 K and with the Curie constant ~10^3 was discovered as a result of submillimeter spectra and dielectric constant measurements [7]. The spontaneous polarization vector of the ferroelectric phase lies in the plane of layers.

In addition to the successive phase transitions described above, a phase transition to weak ferroelectric phase was observed at the temperature about 65 K by authors of [8]. This transition could be explained by using the model of two non-equivalent sublattices proposed by [9]. A very interesting result has been observed by Allakhverdiev et al. [10], after measuring the temperature dependencies of the dielectric constant of $TlGaSe_2$ under bias electric field: the

electrical field dependence of the commensurate phase transition temperature exhibited a behavior peculiar to antiferroelectric crystals.

The detailed investigations of various physical properties of TlGaSe2 at low temperatures, such as optical absorption [11], heat capacity [11, 12] and acoustic emission [13] experiments, revealed additional phase transitions at temperatures about 101-103 K and 246-253 K. As a result of detailed dielectric constant measurements [14-17], two conclusions have been drawn recently: the presence of the incommensurate phase at the temperature interval between 115 K and 242 K and the coexistence of two strong-interacting polar sublattices in the low temperature phase of $TlGaSe_2$.

As it is seen, in spite of a number of experimental results, there was no information about active atomic groups, possible atomic displacements causing the dipole ordering, and the local symmetry changes during the low temperature phase transformations in this compound. As mentioned above, neutron scattering [5] and X-ray studies [6] have shown that the low-temperature ferroelectric phase has a fourfold-commensurate structure. Additionally, the satellite reflections for the incommensurate phase are observed at $\mathbf{q_c}$=(0,0,0.25). Still, any identification of the active group responsible for the mentioned succession of the phase transitions in $TlGaSe_2$ couldn't been done using these experimental methods.

It is known that the Electron Paramagnetic Resonance (EPR) is a well-established method of the investigation for many problems in condensed matter. One of them is the direct identification of the active group for a structural transformation in crystals. EPR experiments utilize paramagnetic probes incorporated into crystal lattice to obtain information about local structural changes in their surroundings. In this article we report on the results of the first investigations of the temperature dependence of EPR spectra of $TlGaSe_2$ compound doped by paramagnetic Fe^{3+} ions, which substituted Ga sites as local probes.

EXPERIMENTAL TECHNIQUES AND RESULTS

$TlGaSe_2$ single crystals were grown in evacuated quartz tubes by using the modified Bridgman method. The iron was added to the growth mixture in amounts corresponding to a molar ratio Fe/Ga of about 2%. The samples for EPR measurements were oriented by x-ray diffraction. The diffraction patterns showed a presence of Fe ions, located periodically in layer planes of the crystal structure. This result allowed us to make the preliminary assumption about the substitution of trivalent Ga atoms by iron impurities.

The EPR spectra were recorded by using Bruker EMX model X-band spectrometer (9.480 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) and (010) planes (directions parallel and perpendicular to the layers respectively). The temperature dependence of EPR spectra was studied in the range of 15-300 K using continuous helium gas flow cryostat made by *Oxford Instruments*. The temperature stability was better than 0.5 K.

In the previous work of some of authors [18], the fine structure of EPR spectra of the paramagnetic Fe^{3+} ions was observed in the Fe-doped $TlGaSe_2$ at room temperature. The spectra were interpreted to correspond to the transitions among the spin multiplet (S=5/2, L=0) of the Fe^{3+} ion, which is split in the local crystal field (CF). Four equivalent Fe^{3+} centers have been observed in the room temperature EPR spectra and the local symmetry of CF at the Fe^{3+} site and the CF parameters were determined. It was established that the symmetry axis of the axial component in the CF is making an angle of about 43 degree with the plane of layers of $TlGaSe_2$ crystal. These experimental results indicate that Fe ions substitute for Ga ions at the center of the $GaSe_4$ tetrahedrons, and the low-symmetry distortion of the CF is caused by Tl ions located in the trigonal cavities between the tetrahedral complexes.

In the present work the EPR spectra of paramagnetic Fe^{3+} doped $TlGaSe_2$ crystals measured in microwave frequency of 9.5 GHz (X band) at various temperatures between 15 K and 300 K for different orientations. The transformation of EPR spectra on lowering the temperature is presented in Fig. 1. The spectra presented in Fig. 1a have been obtained on the application of the static magnetic field in the direction along the crystal layers (in-plane geometry). On the other hand, Fig.1b shows the spectra in out-of-plane geometry-on applying the static magnetic field perpendicular to the plane of the crystal layers. The presented temperatures were selected in accordance with the significant temperature changes. The spectra exhibit two profound changes at the temperatures between 100 K and 120 K. As it is seen from the Fig. 1, these changes are accompanied with both splitting and multiplication of resonance lines. The temperature dependence of the positions of the observed resonance field lines between 25 K and 300 K is shown in Fig. 2a and Fig. 2b for in-plane and out-of-plane geometries respectively. These dependences obviously show the processes of splitting and multiplication of the resonance lines on lowering the temperature and passing through the phase transition temperature point at 110 K. Moreover, the temperature behavior of the resonance lines in the vicinity of the phase transition temperature reminds a well-known temperature behavior of the spontaneous polarization during the ferroelectric phase transition with characteristic critical constants.

So, on considering temperature dependence of EPR spectra of Fe^{3+} ions, we can make a conclusion about the active groups responsible for the phase transitions in $TlGaSe_2$ crystal. As it is mentioned in [18], the low-symmetry distortion of the ligand crystal field on Fe^{3+} site is caused by Tl ions located in the trigonal cavities between the tetrahedral complexes. The observed transformation of the resonance lines, which are clearly attributed to the mentioned distortion, obviously indicates that the ferroelectric ordering in $TlGaSe_2$ is associated with the displacements and ordering of Tl ions located at trigonal cavities. This ordering results in the appearing of anomalies in the dielectric properties as well as the considerable changes in EPR spectra from Fe^{3+} sites.

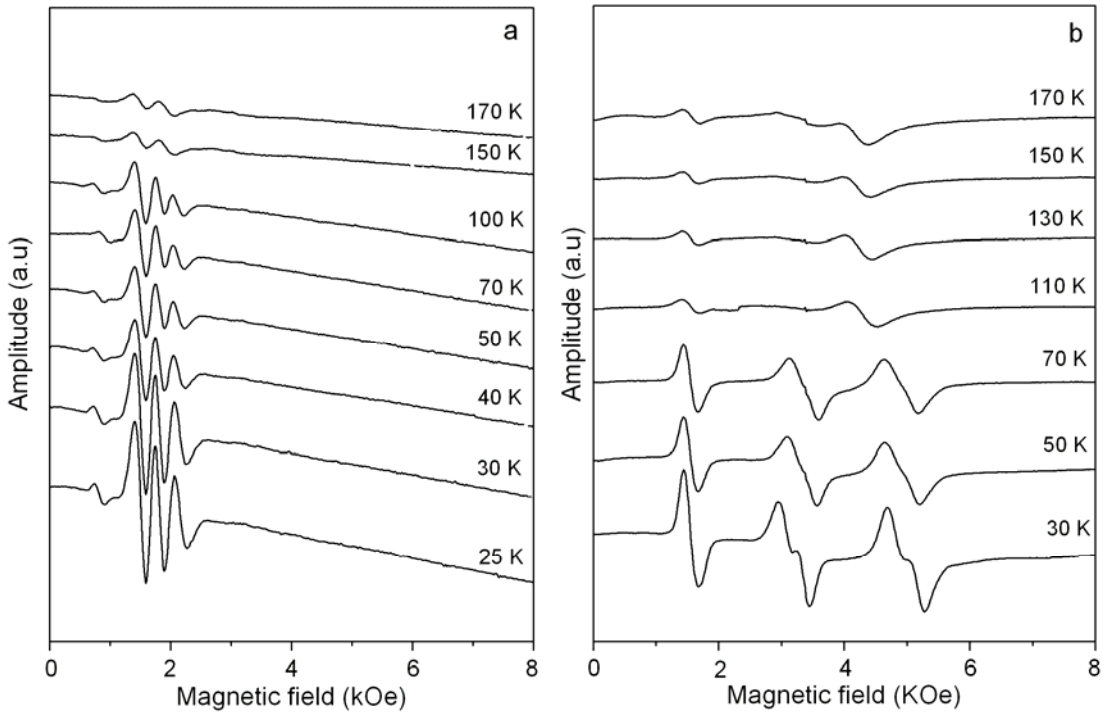

Fig. 1. EPR spectra of Fe^{3+} ions in $TlGaSe_2$ measured at various temperatures for the static magnetic field applied along (a) and perpendicular to the plane of layers (b).

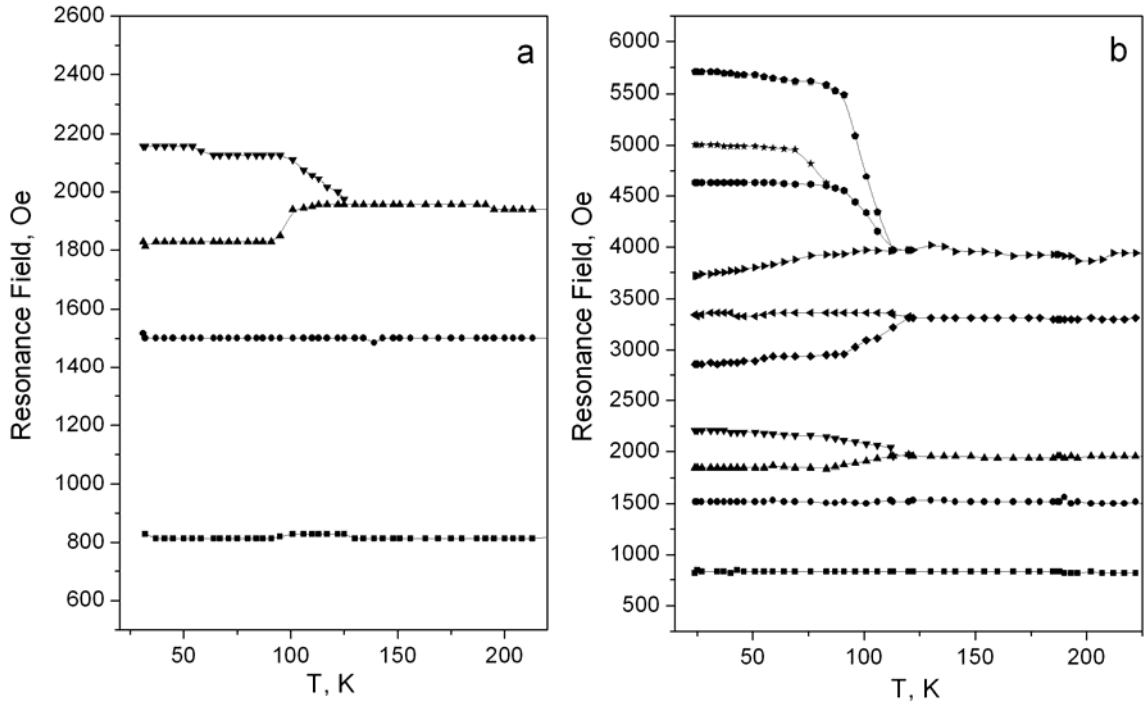

Fig. 2. Temperature dependences of the positions of the observed resonance lines of EPR spectra of Fe^{3+} doped $TlGaSe_2$ crystals for the static magnetic field applied along (a) and perpendicular to the plane of layers (b).

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