Beynəlxalq Konfrans "Fizika-2005"
International Conference "Fizika-2005"
Международная Конференция "Fizika-2005"

İyun
7 - 9   June   2005   №163
Июнь

səhifə
page   632-636
стр.

Bakı, Azərbaycan   **Baku, Azerbaijan**   **Баку, Азербайджан**

ELECTRON PARAMAGNETIC RESONANCE INVESTIGATIONS OF Fe^{3+} DOPED LAYERED $TlInS_2$ AND $TlGaSe_2$ SINGLE CRYSTALS

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$TlInS_2$ and $TlGaSe_2$ single crystals doped by paramagnetic Fe ions have been studied at room temperature by Electron Paramagnetic Resonance (EPR) technique. A fine structure of EPR spectra of paramagnetic Fe^{3+} ions was observed. The spectra were interpreted to correspond to the transitions among spin multiplet (S=5/2, L=0) of Fe^{3+} ion, which are splitted by the local ligand crystal field (CF) of orthorhombic symmetry. Four equivalent Fe^{3+} centers have been observed in the EPR spectra and the local symmetry of crystal field at the Fe^{3+} site and CF parameters were determined. It was established that the symmetry axis of the axial component in the CF is making an angle of about 48 and 43 degree with the plane of layers of $TlInS_2$ and $TlGaSe_2$ crystals respectively. Experimental results indicate that the Fe ions substitute In (Ga) at the center of InS_4 ($GaSe_4$) tetrahedrons, and the rhombic distortion of the CF is caused by the Tl ions located in the trigonal cavities between the tetrahedral complexes.

INTRODUCTION

In recent years there is a growing interest in the ternary layered chalcogenide compounds with a general formula $Tl^+(M^{3+}X_2)^-$, where M=In, Ga and X=S, Se, due to the coexistence of ferroelectric and semiconductor properties, as well as the presence of structural phase transformations in these crystals. $TlInS_2$ and $TlGaSe_2$ belong to a group of ternary layered semiconductors with space group symmetry C_{2h}^6 at room temperature. Structural anisotropy [1,2], successive incommensurate and commensurate phase transitions [3-11], good optical and photoconductivity properties [12] of these compounds made them attractive for researchers and stimulated more detailed investigations of its physical properties using various experimental methods.

According to X-ray diffraction measurements [1,2], the crystal structure of $TlInS_2$ and $TlGaSe_2$ consists of alternating two-dimensional metal-chalcogen layers. The layers are composed of $TlInS_2$ and Ga_4Se_{10} tetrahedron complexes, which represent a combination of four elementary MX_4 tetrahedrons and are linked together by common chalcogen atoms at the corners (Fig.1). The elementary unit cell contains two partially disordered layers, containing successive rows of the tetrahedron complexes, which are turned away from each other by 90^0. Monovalent Tl atoms are in trigonal prismatic cavities resulting from the combination of the M_4X_{10} tetrahedron into a layer. As one can see from the figure, each successive lower layer is shifted along the [010] direction by the length of the edge of the small MeX_4 tetrahedron with respect to the upper layer. As a result, a deviation from the tetragonal symmetry appears. The angle between the monoclinic c angle and the layer plane is about 100^0.

More than two decades have passed since the first publication about the presence of structural phase transitions in ternary layered chalcogenide crystals $TlInS_2$ and $TlGaSe_2$ [3-5]. Since that time these compounds were investigated by using a great number of experimental methods. It has been established that, $TlInS_2$ and $TlGaSe_2$ exhibit a sequence of structural phase transitions, including transitions to an incommensurate (IC) and commensurate (C) phases on lowering the temperature. Neutron scattering [6] and also X-ray studies [7,8] have shown that the low-temperature ferroelectric phase has a fourfold-commensurate structure and the satellite reflections for the

incommensurate phase are observed at $q_i(\delta,\delta,0.25)$. However, one cannot identify the active group responsible for the mentioned succession of the phase transitions in $TlInS_2$ and $TlGaSe_2$ using these experimental methods. 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.
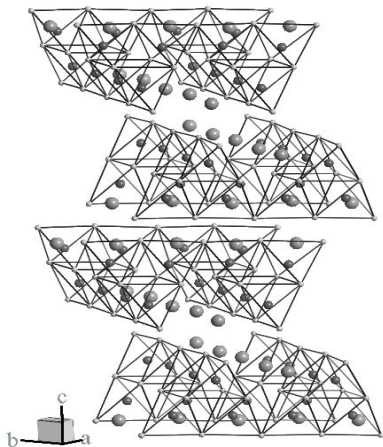

Fig.1. Crystal structure of $TlInS_2$ composed of InS_4 tetrahedrons: ● - Tl ions; ● - In ions; ● - S ions.

Electron Paramagnetic Resonance (EPR) is a well-established method for the direct identification of both the local environment around a substitutional magnetic ion site and the active group for a structural transformation in crystals. EPR experiments utilize paramagnetic probes incorporated into crystal lattice to obtain information about a local environment around a substitutional magnetic ion sites as well as the possible structural changes in their surroundings. The trivalent iron substituted into various crystal structures is known to be a very useful paramagnetic probe providing rich information about the CF, and has been successfully used in a great number of EPR studies of various systems.

In the present work the results of detailed room temperature EPR investigations of $TlInS_2$ compound doped by paramagnetic Fe^{3+} ions substituted at In sites as local probes of the ligand CF has been presented. The results of the low temperature EPR investigations of Fe^{3+} doped $TlInS_2$ crystals will be reported in a separate paper.

EXPERIMENTAL DETAILS

$TlInS_2$ and $TlGaSe_2$ single crystals were grown in evacuated quartz tubes by using the modified Bridgman method. For EPR experiments, iron was added to the growth mixture in amounts corresponding to a molar ratio Fe^{3+}/In^{3+} of about 0.7% and Fe^{3+}/Ga^{3+} of about 2%. The crystals were easily cleaved into the plane-parallel plates along the (001) basal plane, which is parallel to the layers. The morphology of the crystal permits to perform this operation. The quality of the samples and orientation of the crystal planes were controlled by X-ray diffraction measurements.

The EPR spectra were recorded by using Bruker EMX X-band spectrometer (9.8 GHz). The static magnetic field was varied in the range 0-16000 G. The field derivative of microwave power absorption (*dP/dH*) was registered as a function of the static magnetic field (*H*). The angular dependences of EPR spectra were obtained for different orientations of the static magnetic field with respect to the crystalline axes.

RESULTS AND DISCUSSION

Multiline EPR spectra of Fe doped $TlInS_2$ single crystals have been observed at room temperature. The EPR spectra were strongly anisotropic with the resonance fields of the components up to 16 kG. The typical EPR spectra observed on rotation of the static magnetic field in the plane (001) of the plate-like sample ("in-plane" orientation) and in (100) plane ("out-of-plane" orientation) are presented in Fig. 2.
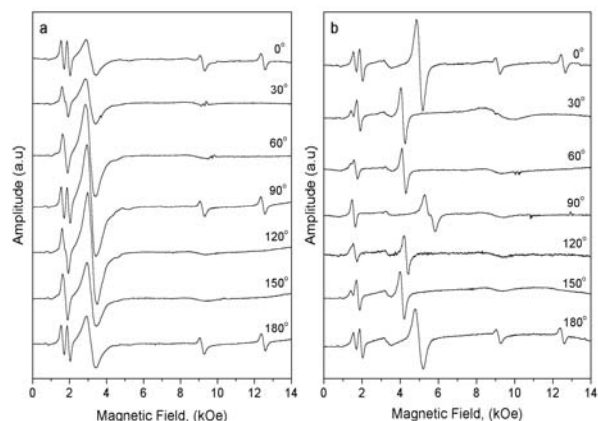

Fig.2. EPR spectra of Fe doped $TlInS_2$ observed for different orientations of the static magnetic field (*H*) on rotating the sample: a) in (001) plane (layer plane); b) in (010) plane.

Angular dependences of the resonance fields of various EPR lines are shown in Figs. 3 and 4. Fig. 3 shows the angular dependence of the resonance fields observed on rotation of the static magnetic field in the plane of the plate-like sample ("in-plane" orientation), while Fig. 3 presents the identical angular dependences on rotation of the sample in two (100) and (010) planes which are perpendicular to the layer plane ("out-of-plane" orientations).
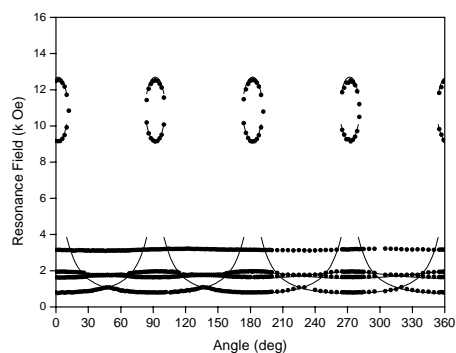
Fig.3. The observed and fitted rotation patterns of the resonant field values for different orientations of the static magnetic field (H) in the (001) plane (in-plane orientation). Full curves are calculated using the spin-Hamiltonian parameters listed in the table.

A strong anisotropy of the EPR lines as well as the fact of their registration even at room temperature unambiguously indicates that the observed EPR spectra is due to the trivalent paramagnetic Fe ions located at the central positions of InS_4 tetrahedrons in the $TlInS_2$ crystal lattice. The rotation patterns, presented in Figs. 3 and 4, show that the EPR spectra originate from different magnetically equivalent Fe^{3+} centers. The rotational pattern observed on applying the static magnetic field in the plane of layers (Fig. 3) revealed a presence of at least two magnetically equivalent centers with symmetry axes nearly perpendicular to earch other. The rotational patterns of the two out-of-plane rotation planes (Figs. 4) allow to make a conclusion about the presence of four centers: two centers with symmetry axes in the (100) plane and nearly perpendicular to each other, and the other ones demonstrating the same symmetry in the (010) plane. The angles between the symmetry directions of the latter centers and the layer plane are about 48^0.

Multiline EPR spectra have been observed at room temperature also for Fe- doped $TlGaSe_2$ single crystal. The EPR spectra were strongly anisotropic with the resonance fields of the components up to 16 kG. The typical EPR spectra observed on rotation of the static magnetic field in the plane (001) of the plate-like sample ("in-plane" orientation) and in (100) plane ("out-of-plane" orientation) are presented in Fig. 5. Angular dependences of the resonance fields of various EPR lines are shown in Figs. 6-8. Fig. 6 shows the angular dependence of the resonance fields observed on rotation of the static magnetic field in the plane of the plate-like sample ("in-plane" orientation), while Figs. 7 and 8 present the angular dependences on rotation of the sample in the (100) and (010) planes which are perpendicular to the $GaSe_4$ layers ("out-of-plane" orientations).
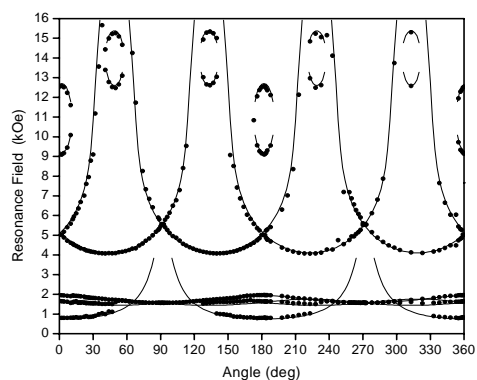

Fig.4. The observed and fitted rotation patterns of the resonant field values for different orientations of the static magnetic field (H) in (100) and (010) planes (out-of-plane orientations). Full curves are calculated using the spin-Hamiltonian parameters listed in the table.
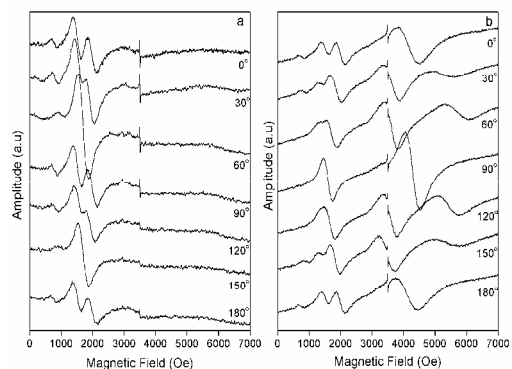

Fig.5. EPR spectra of Fe doped $TlGaSe_2$ observed for different orientations of the static magnetic field (H) on rotating the sample: a) in (100) plane (layer plane); b) in (010) plane.

The strong anisotropy of the EPR lines at room temperature indicates unambiguously that the spectra are due to the trivalent paramagnetic Fe ions in positions of the $TlGaSe_2$ crystal lattice. The rotation patterns, presented in Figs. 6-8, show that the EPR spectra originate from different but structurally equivalent Fe^{3+} centers. The rotational pattern observed on applying the static magnetic field in the plane of layers (Fig. 6) revealed a presence of at least two structuraly equivalent centers with symmetry axes nearly perpendicular to each other. The rotational patterns of the two out-of-plane rotation planes (Figs. 7 and 8) allow to make a conclusion about the presence of four centers: two centers with symmetry axes in the (100) plane and nearly perpendicular to earch other, and the other ones demonstrating the same symmetry in the (010) plane. The angles between the symmetry directions of all the four centers and the layer plane are about 43^0.
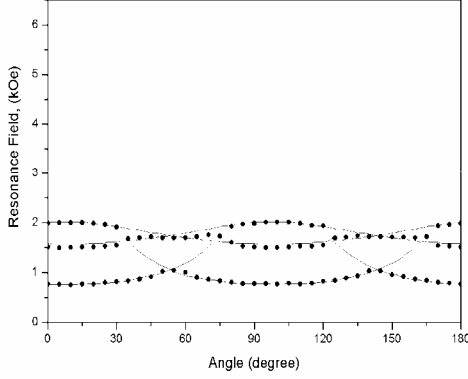
Fig.6 The observed and fitted rotation patterns of the resonant field values for different orientations of the static magnetic field (*H*) in (100) plane (in-plane orientation). Full curves are calculated using the spin-Hamiltonian parameters listed in the table

To obtain parameters of CF at the Fe^{3+} ions a special computer program has been developed to simulate digitally the angular dependences of the resonance fields at an arbitrary rotation plane. According to the CF theory [13,14], the crystalline electric field at a positive ion site has a dominant component arising from an array of surrounding negative charges (ligands). The degeneracy of spin multiplet of the S-state Fe^{3+} ion (S=5/2, L=0) is removed due to the crystal field. Using the equivalent Stevens operators, the energy level splitting of Fe^{3+} ion can be described by the following spin-Hamiltonian:

$$H = H_Z + H_{CF} = b\vec{B}\vec{g}\vec{S} + \sum_{m=0}^{2} B_2^m O_2^m + \sum_{m=0}^{4} B_4^m O_4^m \quad (1)$$

where $S = 5/2$ is the electronic spin and b is Bohr magneton. The first term H_Z accounts for the Zeeman interaction, the second term H_{CF} is the crystal field Hamiltonian. The Stevens operators O_4^m are defined according to Abragam and Bleaney [10]. Taking into account the local symmetry at the Fe^{3+} site to be cubic with a rhombic distortion, we can obtain the following expression for the crystal field Hamiltonian:

$$H_{CF} = B_4\left(O_4^0 + 5O_4^4\right) + B_2^0 O_2^0 + \\ + B_4^0 O_4^0 + B_2^2 O_2^2 + B_4^2 O_4^2 \quad (2)$$

Using the crystal field in the form (2), computer simulations of the EPR spectra of the Fe^{3+} centres in $TlInS_2$ and $TlGaSe_2$ crystals were performed and the spin Hamiltonian parameters were determined. As it is mentioned above, four magnetically equivalent Fe^{3+} ions were assumed and the excellent agreement between experimental and modelled values of the resonant fields has been obtained (Figs. 3,4,6-8).

It was established that there is a very strong crystal field of orthorhombic symmetry at the Fe^{3+} ion positions in the $TlMX_2$ structure. The evaluated parameters, which were then used to fit the observed rotation patterns, are listed in the table.
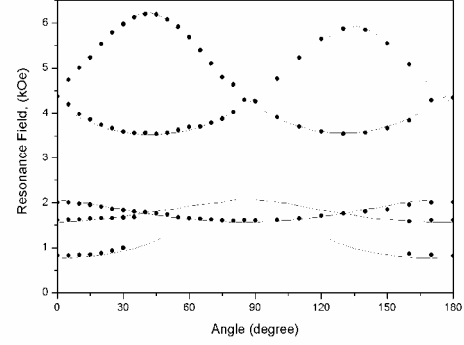

Fig.7. The observed and fitted rotation patterns of the resonant field values for different orientations of the static magnetic field (*H*) in (010) plane (out-of-plane orientation). Full curves are calculated using the spin-Hamiltonian parameters listed in the table.

Crystal	$TlIn_{0.993}Fe_{0.007}S_2$	$TlGa_{0.98}Fe_{0.02}Se_2$
g-factor	2.0 (±0.02)	2.0 (±0.02)
B_2^0, Oe	2400(±100)	2600(±100)
B_2^2, Oe	1700 (±100)	1670 (±100)
B_4	negligibly small	negligibly small
B_4^0	negligibly small	negligibly small
B_4^2	negligibly small	negligibly small

These results indicate that the paramagnetic probes Fe^{3+} substitute for In^{3+} and Ga^{3+} at the central positions of InS_4 tetrahedrons. It is known that perfect MX_4 tetrahedron has a cubic symmetry of the nearest-neighbour ligands (S) at the In site. Therefore, the orthorhombic symmetry of the crystal field can be caused by the influence of the Tl atoms located in the trigonal cavities between the tetrahedral complexes. Fig. 9 shows the Tl position in the trigonal cavities between MX_4 tetrahedrons. It is known [15] that in the layered-chained $TlMX_2$ (M=In, Ga; X=S, Se) systems there is an essential hybridisation of electron wave functions of univalent (Tl) and trivalent (M) ions.

As seen from the figure, in the $TlMX_2$ structure there are two M^{3+} ions in the centers of the two closest MX_4 tetrahedrons, which are the nearest (about 3.9Å) to the Tl^+ ion. There are the other four M ions, which are located approximately in the same plane with distances essentially larger (4.35 Å). Therefore, the experimentally-observed orientation of the principal axes of the crystal field D-tensor (*i.e.* B_2^0, B_2^2 components) with z axis making an appropriate angle (48^0 and 43^0 for $TlInS_2$ and $TlGaSe_2$ respectively) with the layer plane agree well with the direction of Tl-M bond, reported in the literature [16].

Besides, there is another row of Tl ions in the crystal structure of $TlMX_2$, which is directed perpendicularly to the row shown in Fig. 9 and placed near lower tetrahedrons. In this case, the effect of Tl^+ ions, shown in the figure, results in the axial component of the CF on the two nearest M^{3+} ions (with the symmetry axis at 48^0 and 43^0), while the

overall effect of the perpendicular chains of the lower Tl ions provides the rhombic term in the CF in the direction perpendicular to the figure plane.
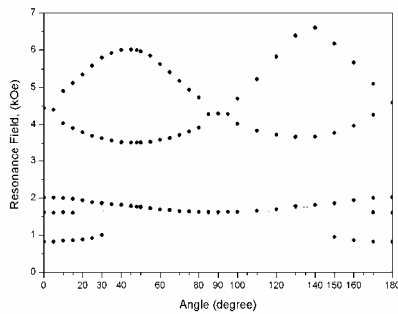

Fig.8 The observed and fitted rotation patterns of the resonant field values for for different orientations of the static magnetic field (*H*) in (001) plane (second out-of-plane orientation). Full curves are calculated using the spin-Hamiltonian parameters listed in the table.

As it is seen from Figs. 7 and 8, there is a slight asymmetry in the rotational patterns of the both above-mentioned sets of the Fe centers. The results of simulations show that this asymmetry may be attributed to a slight misalignment (~5 degree) of the rotational plane with the crystalline (100) or (010) planes. Such misalignment brings to the asymmetry observed in Figs. 3 and 4 and the theoretical curves fit to the experimental data under the appropriate choice of the rotational plane in the simulations.

As it is mentioned above, the unit cell contains two layers containing successive rows of the tetrahedrons. In this frame we can consider the EPR spectra as originating from the Fe^{3+} centers located in different layers, which turned away from each other by 90^0. Moreover, observed broadening of linewidth of EPR lines from Fe^{3+}, which can

be seen from the typical EPR spectra (Figs.2 and 5), can be interpreted by taking into account the presence of two different structural positions of Tl ions in each of thallium rows, as well as two structurally different types of tetrahedrons in each of polyhedron complexes. Thus, there are four possible structural positions of Tl ions in the $TlMX_2$ lattice that provide four equivalent Fe^{3+} centers in EPR spectra. Both the symmetry of CF and number of Fe^{3+} centers observed in experiment agree well with our model.
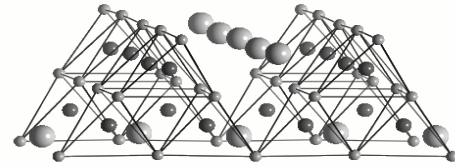

Fig.9. The locations of Tl atoms and Fe^{3+} centers in the crystal structure of $TlInS_2$. ● - Tl ions; ● - Fe^{3+} centers; ● - S ions.

CONCLUSION

EPR of paramagnetic Fe^{3+} ions in the ternary layered compounds $TlInS_2$ and $TlGaSe_2$ has been studied. The spectra were interpreted to correspond to the transitions among spin multiplet of Fe^{3+} ions located at the center of the MX_4 tetrahedra formed by chalcogen atoms. The orthorhombic symmetry of the crystal field (CF) at the Fe^{3+} site was determined. According to the results, the resonance lines originate from the contributions of four structurally equivalent two different types of Fe^{3+} centers localized at different tetrahedron arrays of the crystal structure. The orthorhombic CF symmetry is assumed to originate from Tl ions located in the trigonal cavities between the tetrahedral complexes.

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