EPR spectra of Fe^{3+} centers in layered TlGaSe$_2$ single crystal

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Abstract

A single-crystal TlGaSe$_2$ doped by paramagnetic Fe ions has been studied at room temperature by electron paramagnetic resonance (EPR) technique. The 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. Experimental results indicate that the Fe ions substitute Ga at the center of 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.
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1. Introduction

Electron paramagnetic resonance (EPR) is a very useful method for investigation of the local environment around a substitutional magnetic ion site in crystals. The trivalent iron substituted into various crystal structures is known to be a very useful paramagnetic probe providing rich information about the crystal field (CF), and has been successfully used in a great number of EPR studies of various systems.

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. TlGaSe$_2$ belongs 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 [2–4], good optical and photoconductivity properties [5] of this compound made it 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 TlGaSe$_2$ consists of alternating two-dimensional metal-chalcogen layers. The layers are composed of Ga$_4$Se$_{10}$ tetrahedron complexes, which represent a combination of four elementary GaSe$_4$ 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°. Monovalent Tl atoms are in trigonal prismatic cavities resulting from the combination of the Ga$_4$Se$_{10}$ tetrahedron into a layer. As one can see from the figure, each

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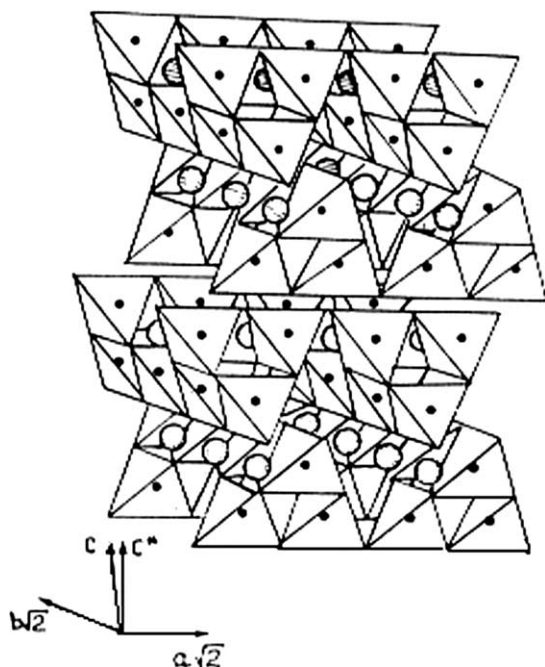*E-mail address:* faik@gyte.edu.tr (F.A. Mikailov).

Fig. 1. Crystal structure of TlGaSe$_2$ built upon GaSe$_4$ tetrahedra: open circles—Tl ions; dots—Ga ions.

successive lower layer is shifted along the [010] direction by the length of the edge of the small GaSe$_4$ 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°.

First EPR investigations of TlGaSe$_2$ compound doped by paramagnetic Fe^{3+} ions were reported by us in Ref. [6]. This paper presents the results of detailed analysis of EPR spectra of Fe^{3+} centers in TlGaSe$_2$, which entered Ga sites as local probes of the ligand CF.

2. Experimental details

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+}/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 0–16,000 G. The field derivative of microwave power absorption (dP/dH) was recorded 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.

3. Results and discussion

Multiline EPR spectra of Fe-doped TlGaSe$_2$ single crystal 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. 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 Figs. 3 and 4 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).

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. 3–5, 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. 3) revealed a presence of at least two structurally equivalent centers with symmetry axes nearly perpendicular to each other. The rotational patterns of the two out-of-plane rotation planes (Figs. 4 and 5) 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 all the four centers and the layer plane are about 43°.

In order to obtain the crystal field parameters at the Fe^{3+} sites 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 [7,8], 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 splittings of Fe^{3+} ion can be described by the following spin-Hamiltonian:

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

where $S=5/2$ is the electronic spin and β is Bohr magneton. The first term H_Z accounts for the Zeeman interaction, the