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ELECTRON SPIN RESONANCE SPECTRA OF Fe^{3+} IONS IN $SrLaAlO_4$ AND $SrLaGaO_4$ HIGH-T_c SUBSTRATES

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New results concerning paramagnetic defects in $SrLaAlO_4$ and $SrLaGaO_4$ high-T_c substrates connected with unavoidable impurity Fe^{3+} are reported. The identification was checked by measuring the spectra in $SrLaAlO_4$ crystals intentionally doped with 0.5 at.% Fe. Angular dependences of three lines were distinguished at X-band frequency in the temperature range from 4 K to 300 K. We attribute these lines to the transitions inside the doublets $\pm 1/2$, and "forbidden" doublets $\pm 3/2$, $\pm 5/2$, respectively. By diagonalization of spin-Hamiltonian, parameters $|D| > 1.2$ cm^{-1}, $|E| \approx 0.1$ cm^{-1} and $g_x = g_y = g_z = 1.987(13)$ for $SrLaAlO_4$ and $SrLaGaO_4$ were calculated and within the margin of error they were of the same value.

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1. Introduction

Single crystals of $SrLaAlO_4$ (SLA) and $SrLaGaO_4$ (SLG) are considered as the promising substrates for HTSC films. There is little information in literature about transition metal impurities in both SLA and SLG crystals. Only a few of them such as Nd^{3+} [1] and Cr^{3+} [2] have been identified and studied by optical absorption, luminescence and ESR measurements [3, 4].

Both, SLA and SLG, compounds crystallize in a tetragonal structure similar to that of K_2NiF_4. This structure has $I4/mmm$ space group symmetry [5]. Crystal lattices create a linked oxygen octahedral with Al or Ga ions in their centre and with Sr and La ions located between them. Therefore, each Al or Ga ions has six oxygen ions in its first coordination zone and nine Sr or La ions in the second coordination zone. Additionally, the usual assumption has been made about random distribution of Sr and La ions [5]. The iron ions substitute the aluminium or gallium ions in this structure [6].

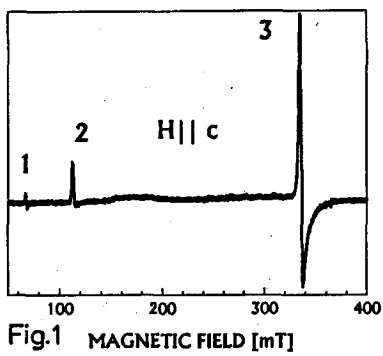
This paper reports on ESR studies on iron doped SLA and SLG crystals. It will be shown that single Fe^{3+}-ion transitions provide a satisfactory interpretation of observed ESR spectra.

2. Experiment

Single crystals of SLA and SLG were grown by the Czochralski technique with the use of iridium crucible. Iron-doped crystals have been grown by adding Fe_2O_3 to the alloy. The obtained iron concentration was 0.1 at.% for SLA and SLG crystal contains iron impurity lower than 10^{-3} at.%. The samples typically $3.5 \times 3.5 \times 2$ mm^3 were measured in a BRUKER ESP-300 ESR spectrometer (X-band). The spectrometer was equipped with a helium flow cryostat type ESR-900 Oxford Instruments. The ESR lines were observed in the temperature range from 4 K to 300 K.

3. Results and discussion

Figure 1 shows typical ESR spectra of an iron-doped SLA sample recorded with the magnetic field which is parallel to "c" crystal direction. This spectrum consists of a strong asymmetric line and two weaker lines, their line width $\Delta H = 1.5 \div 2.0$ mT. The ESR spectra of iron-doped SLA and SLG crystals looked similarly.



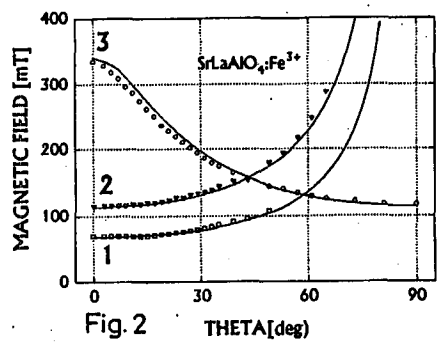


Fig. 1. ESR spectrum of Fe^{3+} in $SrLaAlO_4$ recorded with the magnetic field which is parallel to "c" crystal direction, $T = 18$ K.
Fig. 2 ESR angular variation at 18 K of: 1. $|+5/2\rangle \rightarrow |-5/2\rangle$, 2. $|+3/2\rangle \rightarrow |-3/2\rangle$, 3. $|+1/2\rangle \rightarrow |-1/2\rangle$, electronic transition of the Fe^{3+} ions in $SrLaAlO_4$. Theoretical results (solid line) were calculated by using the following ESR parameters: $g = 1.987(13)$, $|D| > 1.2$ cm^{-1}, $|E| \approx 0.1$ cm^{-1}.

The ESR spectra of Fe^{3+} in SLA crystals were observed by the authors [7] in undoped SLA crystals grown by the Czochralski method. In all these crystals the concentration of Fe^{3+} was lower than 10^{-3} at.%. The ESR spectrum, related to the residual concentration in SLG crystals, is also observed. In both cases the sources of the trace amount of Fe^{3+} in undoped crystals are the starting materials.

The identification of Fe^{3+} spectrum was done by measuring Fe^{3+} spectra in intentionally doped SLA crystals [8]. In these crystals the angular dependence (see Fig. 2) of three lines are attributed to Fe^{3+} ($3d^5$, $S = 5/2$). The lines of "allowed" doublet $\pm 1/2$, and "forbidden" $\pm 3/2$, $\pm 5/2$ transitions were observed. To make

sure that the observed lines are really connected with the above doublets, three different microwave frequencies were used to check that ESR lines shift according to the slope characteristic of these doublets. The results are shown in Table.

TABLE

ESR lines shift.

Frequencies [GHz]	Line No. 1 $(-5/2 \rightarrow +5/2)$ [mT]	Line No. 2 $(-3/2 \rightarrow +3/2)$ [mT]	Line No. 3 $(-1/2 \rightarrow +1/2)$ [mT]
9.351	67.1	113.14	334.2
9.412	67.6	114.20	336.4
9.637	69.0	116.20	343.9

The spin-Hamiltonian $\mathcal{H} = g\beta \boldsymbol{H}\cdot\boldsymbol{S} + D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2)$ was used to fit experimental data with theoretical calculations. The best fitting was obtained with the following parameters: $g_{\parallel} = g_{\perp} = 1.987(13)$, $|D| > 1.2$ cm^{-1}, $|E| \approx 0.1$ cm^{-1}. This is shown in Fig. 2, where on the background of the experimental values the solid line indicates the results of calculations.

The presence of $E(S_x^2 - S_y^2)$ term mixes the states and according to Ref. [9] the forbidden $\pm 3/2$ and $\pm 5/2$ transitions can be observed with intensity proportional to the ratio E/D. In Ref. [10] such transitions were observed in $CdWO_4$ for Fe^{3+} ion.

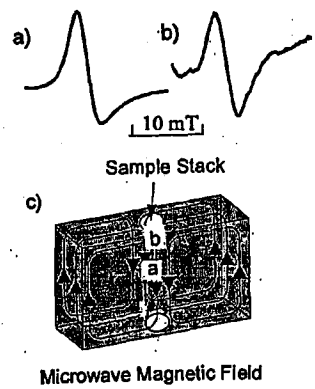


Fig. 3. The line shape of electronic transition $|+1/2\rangle \rightarrow |-1/2\rangle$ for $H \| c$-axis on the position of the sample in the microwave cavity TE_{102}, (a) sample localised in the centre of cavity, (b) sample localised at the edge of cavity according to the symbols in (c), $T = 18$ K.

The influence of the microwave magnetic and electric field on the line shape of the line $+1/2 \rightarrow -1/2$ is presented in Fig. 3. In "a" position the line is a superposition of the transitions induced by microwave magnetic field and inhomo-

geneous electric crystal field, which is reflected in an asymmetrical shape of the line. In "b" position transitions are induced by the dominant microwave electric field and the symmetric line shape is observed as a consequence. A similar dependence of the ESR line shape on microwave magnetic and electric field was studied in Refs. [11, 12].

4. Conclusions

From the above experiments it can be seen that iron can be introduced into SLA and SLG crystals. The Fe^{3+} ions substitute the Al^{3+} or Ga^{3+} ions in these structures.

The influence of the microwave magnetic and inhomogeneous electric field is reflected in the asymmetrical shape of the line. It results from a structural disorder in the crystal lattice. Local perturbations in the crystal field at Al or Ga ion sites, which cause the lack of inversion symmetry, can be connected with the random distribution of Sr^{2+} and La^{3+} ions among oxygen octahedrals.

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