ESR Investigation of Gd$^{3+}$ Ion Introduction into the Structure of Simple and Double Tungstates

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Abstract. In this paper the spectra of Gd$^{3+}$ ions studied by electron spin resonance (ESR) in four types of tungstate crystals KY(WO$_4$)$_2$, CdWO$_4$, CsLa(WO$_4$)$_2$ and La$_3$(WO$_4$)$_4$ are discussed. The tungstate crystals were grown by the low-temperature gradient Czocharalski technique with Gd$_2$O$_3$ addition in melt. The estimation of spin Hamiltonian (SH) parameters was realized using an original simulation program developed. The parameters of crystalline field in oxide crystals are comparable with Zeeman interaction so the solution of the Schrödinger equation was realized numerically. We have estimated 36 SH parameters from ESR angular diagrams of Gd$^{3+}$, including $g_x$, $g_y$, $g_z$, $g_\theta$, $B'_m$, $C'_m$ (where $i = 1, ..., 6$), $B''_m$, $C''_m$ (where $m = 2, ..., 6$, $n = 0$ for $C''_2$, ..., $m$), and the Euler angles. The positions of Gd$^{3+}$ ions in the crystal structures, the charge compensation and the influence of lattice parameters on the SH parameters $B''_2$ and $B''_3$ are discussed in this paper as well.

1 Introduction

The Gd$^{3+}$ ions are rather convenient objects to be investigated by the electron spin resonance (ESR) technique because this ion is one of the few lanthanides with ESR spectra observable in a wide temperature range (including room temperature). This property favored the investigations of these f-ions in different crystal matrices and there are a lot of references in literature on the Gd$^{3+}$ ions substituted into the crystal structure of tungstates CdWO$_4$ [1], CaWO$_4$ [2], SrWO$_4$ [3], BaWO$_4$ [4], PbWO$_4$ [5] and molibdates KY(MoO$_4$)$_2$ [6], MgMoO$_4$ [7], CaMoO$_4$ [8], CdMoO$_4$ [9], SrMoO$_4$ [10], BaMoO$_4$ [11]. Note that in spite of the gadolinium ion model in the ionic surrounding being theoretically worked out well, the data provided in the above papers have very low accuracy, seemingly because the authors used in calculations the perturbation theory at the edge of its applicability. For example, refs. 1 and 12 are concerned with the theoretical calculations of the zero-field splitting using the point-charge model.

The tungstate crystals are of interest because of their active optical properties which give an opportunity to use these crystals as nonlinear optical devices, in wavelength converters, scintillators and laser applications (the literature publi-
cations on laser applications are mainly restricted to KGd(WO₄)₂ crystals). The Gd³⁺ ion has a half-filled f-shell so it is paramagnetic but a magnetically concentrated system such as KGd(WO₄)₂ shows strong exchange coupling which impedes the analysis of single-ion magnetic interaction effects. Some magnetic “dilution” is necessary to investigate these effects which could be done by substituting gadolinium ions for nonparamagnetic isovalent ions or by isomorphic substitution of gadolinium ions into nonparamagnetic crystals during their growth.

This paper presents the results of the ESR investigation of CsLa(WO₄)₂ and KY(WO₄)₂ crystals doped with gadolinium ions. The features of the Gd³⁺ substitution into the structure of La₂(WO₄)₃ and CdWO₄ are also presented when three- and two-valent cations are replaced by the gadolinium ions. This could be considered as a paramagnetic probe to investigate the local features of the crystal field in the two- and three-valent ion position. Several issues of the nonisovalent substitution of the two-valent cation for the gadolinium ion in the tungstate crystal lattice are considered as well.

2 Experimental

CsLa(WO₄)₂, KY(WO₄)₂, La₂(WO₄)₃, and CdWO₄ crystals were grown by low-gradient Czochralski technique. All crystals were doped with gadolinium by adding the gadolinium oxide Gd₂O₃ to the initial melt. The concentration of gadolinium ions in different crystal specimens was from about 10 to about 10000 ppm. The ESR spectra were recorded on a computerized Varian E109 spectrometer at 9.5 and 35.5 GHz and at 300 and 77 K. The crystal specimens were oriented by the X-ray diffractometry technique and then were cut along definite crystallographic planes to allow goniometric measuring of ESR angular diagrams.

To analyze the complex ESR spectra of gadolinium ions in the oxygen surrounding we have developed special computer programs which allow one to simulate ESR spectra avoiding the use of the perturbation theory and to automatically obtain the optimized spin Hamiltonian (SH) parameters of a paramagnetic center [13]. The input parameters are the electronic spin of a paramagnetic center, presumed form of the paramagnetic center’s SH (chosen by taking into account the electronic spin and the symmetry of the paramagnetic center) and the principal directions of tensors involved in SH. The program diagonalizes SH thus calculating the energy levels and corresponding wave functions, calculates the simulated ESR spectra and then by automatically varying the SH parameters optimizes them to achieve the optimal agreement between experimental and simulated ESR angular diagrams. For simulations we took SH of the triclinic symmetry:

\[ \mathcal{H} = (g_x \mu_B H_x S_x + g_y \mu_B H_y S_y + g_z \mu_B H_z S_z) + (g_1 \mu_B H_x O_1^1 + g_2 \mu_B H_y O_1^2)
\]
\[ + (g_3 \mu_B H_z O_3^0 + g_4 \mu_B H_x O_3^1 + g_5 \mu_B H_y O_3^2 + g_6 \mu_B H_z O_3^3) + (B_0^0 O_0^0 + B_1^0 O_1^0)
\]
\[ + C_1^1 \Omega_1^1 + B_2^2 O_2^2 + C_2^2 \Omega_2^2) + (B_4^4 O_4^0 + B_3^1 O_3^1 + C_2^3 \Omega_3^1 + B_4^3 O_3^2 + C_2^4 \Omega_2^3 + B_4^6 O_4^3
\]

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