An EPR Study of the V^{4+} and Cu^{2+} Ions in Single Crystals of β-$Mg_2V_2O_7$ and α-$Zn_2V_2O_7$: non-coincident $\tilde{\mathbf{g}}^2$and $\tilde{A}^2$ Tensors

S.K. Misra[1], S.I. Andronenko[2]

[1]Physics Department, Concordia University, Montreal, Canada
[2]Institute of Physics, Kazan Federal University, Kazan, Russian Federation

e-mail: SIAndronenko@kpfu.ru

The angular variations of V^{4+} and Cu^{2+} EPR spectra in β-$Mg_2V_2O_7$ and α–$Zn_2V_2O_7$ were recorded for orientations of the external magnetic field in three mutually perpendicular planes at 120 K and 295 K, as well as in the temperature range from 110 to 295 K at some chosen orientations of the magnetic field. The principal values of the $\tilde{\mathbf{g}}^2$ and $\tilde{\mathbf{A}}^2$ tensors for the V^{4+} and Cu^{2+} ions, as well as the orientation of their principal axes were determined from the angular variations of the EPR line positions in three mutually perpendicular planes, using a rigorous least squares fitting procedure, using the eigenvalues and eigenvectors of the SH matrix, especially adapted to the case of non-coincident principal axes of the $\tilde{\mathbf{g}}^2$ (Zeeman) and $\tilde{\mathbf{A}}^2$ (hyperfine interaction) -tensors for the monoclinic and triclinic space-group symmetries in β-$Mg_2V_2O_7$ and α–$Zn_2V_2O_7$, respectively [1,2], varying the appropriate Euler angles relating the non-coincident principal axes of the $\tilde{\mathbf{g}}^2$ and $\tilde{\mathbf{A}}^2$-tensors. The principal values of the $\tilde{\mathbf{g}}^2$-and $\tilde{\mathbf{A}}^2$-tensors of the Cu^{2+} ion in these crystals are found to have similar values, which implies that the Cu^{2+} ion has the same $|0\rangle$ ground state in the two crystals. The orientations of the principal axes the $\tilde{\mathbf{g}}^2$ and $\tilde{\mathbf{A}}^2$ -tensors of the Cu^{2+} ions are found to be non-coincident with each other. This is because the Cu^{2+} ion in β-$Mg_2V_2O_7$ is 6-fold coordinated, whereas it is 5-fold coordinated in a trigonal bipyramidal configuration in α–$Zn_2V_2O_7$. The principal values of the $\tilde{\mathbf{g}}^2$-and $\tilde{\mathbf{A}}^2$-tensors of the Cu^{2+} and V^{4+} ions at 120 K are listed below.

Cu^{2+}	g_z	g_x	g_y	A_z (GHz)	A_x (GHz)	A_y (GHz)
$Mg_2V_2O_7$	2.015±0.001	2.283±0.001	2.358±0.001	0.24±0.01	0.13±0.01	0.0±0.01
$Zn_2V_2O_7$	1.999±0.001	2.283±0.001	2.358±0.001	0.26±0.01	0.17±0.01	0.0±0.01

The principal values of the $\tilde{\mathbf{g}}^2$ and $\tilde{\mathbf{A}}^2$ -tensors of the V^{4+} ions are the same in the two crystals. The orientations of the principal axes the $\tilde{\mathbf{g}}^2$ and $\tilde{\mathbf{A}}^2$ -tensors of the V^{4+} ions are found to be non-coincident, but similar, to each other in α-$Zn_2V_2O_7$ and β-$Mg_2V_2O_7$ crystals [3].

V^{4+}	g_z	g_x	g_y	A_z (GHz)	A_x (GHz)	A_y (GHz)
$Mg_2V_2O_7$	1.932±0.001	1.969±0.001	2.002±0.001	0.49±0.01	0.17±0.01	0.16±0.01
$Zn_2V_2O_7$	1.932±0.001	1.976±0.001	2.011±0.001	0.50±0.01	0.19±0.01	0.18±0.01

The V^{4+} ion is tetrahedrally coordinated in both crystals with the Γ_3 doublet being the ground state, which for the V^{4+} ions in β-$Mg_2V_2O_7$ and α-$Zn_2V_2O_7$ are found to be similar, because the local environments of V^{4+} ions in the corresponding VO_4 configurations are almost identical in the two crystals.

This work was supported by NSERC (SKM) and the Ministry of Education and Science of Russian Federation, project allocated to Kazan Federal University (#3.2166.2017/4.6).

[1] S.K. Misra, J. Magn. Reson. **23**, 403 (1976).
[2] S.K. Misra, Physica B **151**, 433 (1988).
[3] S.K. Misra, S.I. Andronenko, Magn. Reson. Solids **20**, 18101(8p) (2018).