Theoretical Investigations of the Local Structure and the EPR Parameters of Mn$^{4+}$ in LiF:U:Mn Crystal

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The local structure and the EPR parameters (zero-field splitting $D$, $g$ factors $g_\parallel$ and $g_\perp$ and hyperfine structure constants $A_\parallel$ and $A_\perp$) of Mn$^{4+}$ in LiF:U:Mn crystal have theoretically been investigated by using the perturbation formulas of the EPR parameters for a 3d$^3$ ion in trigonally distorted octahedra. In this trigonal Mn$^{4+}$ center, three U$^{6+}$ ions locate on (1,1,0), (1,0,1) and (0,1,1) sites, each surrounded by six O$^{2-}$ ions. Thus, the studied system is characterized as the Mn$^{4+}$ associated with one host F$^-$ triangle, one O$^{2-}$ triangle and an additional equivalent F$'$ triangle containing the three U$^{6+}$ ions, i.e. an [MnF$_3$O$_3$F$_3$]$^{8-}$ cluster. The central Mn$^{4+}$ impurity is found to shift towards the oxygen triangle along the $C_3$ (or [111]) axis by an amount $\Delta Z$ ($\approx$ 0.29 Å) due to the strong electrostatic attraction between the Mn$^{4+}$ and the oxygen triangle (and also the additional equivalent F$'$ triangle), which increases the trigonal distortion of the Mn$^{4+}$ center considerably. The calculated EPR parameters based on the above displacement $\Delta Z$ agree reasonably with the observed values.

Key words: Defect Structure; Electron Paramagnetic Resonance (EPR); Crystal-field Theory; Mn$^{4+}$; LiF.