Charge localization in La, Pr and Nd substituted Sr hexaferrites

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In the M-type hexagonal ferrite $SrFe_{12}O_{19}$ ferric cations form five magnetic sublattices, denoted as 2a, 2b, $4f_{IV}$, $4f_{VI}$ and 12k. The magnetic structure is collinear: moments of 2a, 2b and 12k are parallel ($4f_{IV}$ and $4f_{VI}$ antiparallel) to the overall magnetization with easy direction along the hexagonal c-axis. Substitution of divalent Sr for a trivalent one (La, Nd, Pr, Sm, Eu, Gd, . . .) produces an excess valence electron and leads to changes in valence states of ferric ions. From measurements of magnetocrystalline anisotropy and total magnetic moment Lotgering [1] deduced that Fe^{2+} should localize in octahedral 2a site at low temperatures and proposed that the increased magnetic anisotropy is due to single ion contribution of Fe^{2+} in 2a sites. Since then the picture of full (or strongly preferred) Fe^{2+}(2a) localization was supported by various local hyperfine methods, however, the mechanism of increased magnetic anisotropy can be experimentally clarified only indirectly. Theoretical description of the increased anisotropy is lacking, since the solution corresponding to Fe^{2+}(2a) has not been achieved until now. The calculations of electronic structure resulted in a delocalized solutions with excess charge contained in the interstitial space or smeared over all iron sites [2-3].

Using electron structure calculations we model the Fe^{2+} localization in 2a sites of La, Nd, and Pr hexaferrites. Orbital potential is employed to stabilize various orbital states, and thus obtain more than one scf solution. The desired localized solution is found to be energetically favourable compared to the delocalized one, for all used substituting trivalent atoms. This is also supported by ^{57}Fe nuclear magnetic resonance experiments where the intensity of Fe^{3+}(2a) line decreases linearly with increasing concentration of trivalent large ion. The single-ion contribution to magnetocrystalline anisotropy of the hexaferrites is calculated using the force theorem approach, while the dipolar contribution is obtained by direct summation and is found to be much smaller. The results show that the localization is responsible for the increased anisotropy of LaM, compared to SrM. We discuss the details of the charge localization and the mechanism leading to increased anisotropy and also explain the strong decrease of anisotropy in LaM with increasing temperature (in contrast with constant character in case of SrM).

[1] F. K. Lotgering, J. Phys. Chem. Solids 35, 1663 (1974).
[2] P. Novák et al., Eur. Phys. J. 43, 509 (2005).
[3] M. Küpferling et al., J. Appl. Phys. 97, 10F309 (2005).