

Giant Magnetoelectricity in Aluminium Substituted Y-Hexaferrites

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The electron structure of Al containing Y-hexaferrite that exhibits the giant magnetoelectricity is calculated. Results show strong preference of Al for octahedral sites. Orbital moment of some of the iron ions is found to be unusually large.

PACS numbers: 75.85.+t, 71.20.Ps, 75.50.Gg

1. Introduction

In a recent paper Chun et al. reported a giant magnetoelectricity (ME) in the Al substituted Y-hexaferrite $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2(\text{Fe}_{1-x}\text{Al}_x)_{12}\text{O}_{22}$ [1]. For an optimum $x = 0.08$ the ME effect is by an order of magnitude stronger and it occurs at much lower external magnetic field compared to the parent compound, in which ME was found earlier by Kimura et al. [2]. The surprising enhancement of ME by the Al substitution was tentatively ascribed to a decrease of the magnetocrystalline anisotropy, which keeps the magnetization in the plane perpendicular to the hexagonal axis. The working hypothesis of Chun et al. is that practically all Al ions substitute Fe in an octahedral sublattice 18h in which the Fe position is off-center. There are three other octahedral sublattices 3a, 3b and 6c filled by Fe in the parent compound. Two tetrahedral sublattices 6c₁ and 6c₂ are occupied by Fe and Zn. Similarly as in GaFeO_3 [3] the off-centricity may lead to a large orbital moment from which presumably the anisotropy originates. The effect of Al may then be either direct (decrease of the number of Fe, possessing large orbital momentum), or indirect by diminishing the off-centricity.

In the present contribution we find out to which extent the above described scenario is supported by an *ab initio* calculation of the electron structure. In particular the total energy of the hexaferrites containing Al in different sublattices are compared, the off-centricity of the Fe is evaluated and the orbital momentum of iron is calculated.

2. Method

The problem is complicated by the fact that there is a lot of disorder in the system in question: Ba and Sr enter the same sublattice and the two tetrahedral sublattices

are partially occupied by Zn and partially by Fe. Similarly as in our paper [4] we circumvented this problem by considering $(\text{Ba}_{1-y}\text{Sr}_y)_2\text{Zn}_2(\text{Fe}_{1-x}\text{Al}_x)_{12}\text{O}_{22}$ system for three Sr concentrations $y = 0, 0.5, 1$ and two different distributions of (Fe,Zn). This distribution is characterized by parameter γ , which is likely to lie between 0.6 and 0.9 [5]. To preserve as high symmetry as possible the calculations were done for $\gamma = 0.5$ and 1. The WIEN2k package [6] was used and in order to describe better the strong correlation of the 3d electrons of Fe and Zn the GGA+*U* method was employed. The computational details are more completely described in Ref. [4]. The substitution of aluminium was modelled by replacing in the unit cell one Fe by Al. This corresponds to Al concentration $x = 0.0833$, which is close to the optimal value 0.08 found by Chun et al. [1]. The total energy was then minimized by varying the positions of the atoms.

3. Results and discussion

For all six combinations of y and γ we found that the lowest total energy corresponds to Al in octahedral sublattice 3b. Very close, however, is the energy of substitution in the sublattice 18h (Fig. 1). The energy cost of Al substitution in remaining four sublattices is higher by at least 0.4 eV. Because there are six times more 18h than 3b sites, the difference ≈ 0.05 eV of the total energies may actually mean that at the temperature of crystal growth most of Al ions enter sublattice 18h and the calculation thus supports the assumption made by Chun et al. [1].

The Fe ions on 18h sites are off-centered, the displacement being along the hexagonal axis. We characterize the off-center shift by parameter ω :

$$\omega = \sum_{j=1,6} [z(\text{O}_j) - z(\text{Fe})],$$

where $z(\text{O}_j)$ is the z coordinate of the nearest oxygen neighbor of the Fe in question. ω was evaluated for all six combinations of y and γ of the parent compound as

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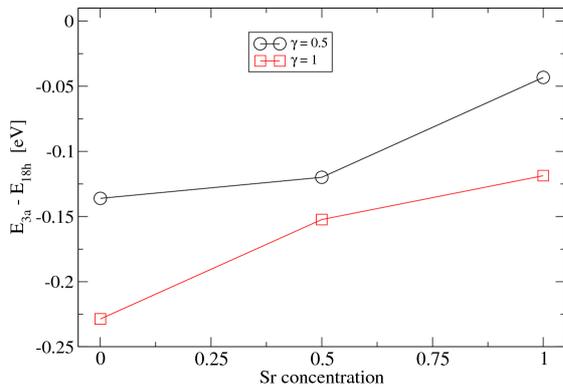


Fig. 1. The energy difference per formula unit of exchanging one Fe atom by Al in the sublattice 18h and 3b.

well as for these six combinations with Al in 18h sublattice. We found strong dependence of ω on (Fe,Zn) distribution (absolute value of ω for $\gamma = 1/2$ was about 0.05 nm, while for $\gamma = 1$ it was approximately four times smaller). The dependence of ω on the Sr concentration is much weaker and also presence of Al has only small and unsystematic effect. The quenching of the off-center shift by presence of Al is therefore not supported by our calculation.

All above calculations were performed without the spin-orbit coupling (soc). In order to calculate the orbital moment the iteration procedure was first converged without soc, afterwards for several directions of the magnetization a single iteration was run that included soc and the orbital moment was determined. The magnitude of orbital moment \mathbf{l} depends on both γ and x , and, to a smaller extent, on the direction of the magnetization. In the unsubstituted compounds it may reach large value, considering that nominally all iron ions are trivalent with half-filled 3d shell. The biggest $|\mathbf{l}| = 0.23$ was found for $y = 0.5$, $\gamma = 0.5$ and Fe on the 6c sublattice, for Fe on 18h sites $|\mathbf{l}|$ ranges between 0.05 and 0.14. The substitution of Al leads to a significant reduction of $|\mathbf{l}|$ by $\approx 50\%$ for

Fe on the 6c and 18h sites. We did not analyze the reason for the reduction, but it is likely to be connected with the lower local symmetry in the Al substituted systems.

4. Conclusions

The results obtained corroborate two of the assumptions made by Chun et al.: large preference of Al for the octahedral sites and presence of iron ions with unusually large orbital moment, which is reduced by the Al substitution. To find out whether this leads to a smaller magnetocrystalline anisotropy is the subject of our ongoing investigation.

Acknowledgments

The work was supported by project IAA100100803 of the Grant Agency of the AS CR.

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