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SEMINAIRE DMONS - Axes Magnétisme et Matériaux

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Co occupied site control to develop next generation ferrite magnets

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Base materials of hard ferrite magnets are ferrimagnetic M-type ferrites AFe$_{12}$O$_{19}$ (A = Sr, Ba, Ca, …) with five crystallographycally different Fe sites; majority-spin 12k, 2a and 2b sites and minority-spin 4f$_1$ and 4f$_2$ sites. When the Fe sites are replaced with a small amount of Co and the A site with La for charge compensation, the coercivity and magnetization increase together, and the magnets have been commercialized as high-performance ferrite magnets [1]. The performance is improved because Co has an orbital component in the magnetic moment and mainly occupies minority-spin sites. However, it is known that the degree of performance improvement associated with Co substitution depends on the A ion. This is reminiscent of the fact that Co occupied sites or the Co site distribution differs depending on the A ion. Previous studies have shown that Co mainly occupies the 4f$_1$ minority-spin site and the 12k and 2a majority-spin sites [2], but we found that only Co occupying the 4f$_1$ site contributes to the improvement of uniaxial magnetic anisotropy [3]. Therefore, it is expected that the difference in performance for the same amount of Co depending on the A ion is due to the difference in the 4f$_1$ site occupancy of Co. In this study, Co distribution was experimentally evaluated by ^{59}Co-NMR and Co preferentially occupied sites were evaluated by DFT calculations for systems with different A ions.

La–Co co-substituted M-type ferrites AFe$_{12}$O$_{19}$ (A = Ca, Sr, and Ba, ion size is $Ca^{2+} < Sr^{2+} < Ba^{2+}$) with Co composition around 0.2 were subjected to ^{59}Co-NMR. The results show that Co occupies the 4f$_1$, 2a, and 12k sites, and that the smaller A, the more Co tends to occupy the 4f$_1$ minority-spin site, which is effective in enhancing uniaxial anisotropy. Furthermore, DFT calculations of non-doped AFe$_{12}$O$_{19}$ and the supercells (2 × 2 × 1 of the unit cell) in which 1/96 of Fe^{3+} is replaced by Co^{2+} were performed to predict the stable structure and the Co occupation sites. The results show that regardless of A, Co is most stable when it occupies the 4f$_1$ site, followed by the 2a and 12k sites with energy differences on the order of 100 meV, and that Co practically does not occupy the 2b and 4f$_2$ sites. As the A ion becomes smaller, the distribution of energy when Co occupies each Fe site tends to broaden, and the Co occupancy of the 4f$_1$ site also increases. The site selectivity of Co can be roughly explained as a result of the difference in uniaxial strain along the c axis associated with the difference in A, but the influence of A ions differs between the R and S blocks in the unit cell, and local strain also has a secondary effect on the Co distribution.

Based on the above results, to improve the performance (anisotropy and magnetization) of La-Co co-substituted M-type ferrite magnets with limited Co content, it is effective to select as small A ions as possible to concentrate Co in the tetrahedral coordination of the 4f$_1$ site.

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References

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