Electronic structure of light rare earth permanent magnets

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Despite intensive efforts to develop permanent magnets whose performances exceed that of the $Nd_2Fe_{14}B$ magnet, no essentially novel magnet has been developed so far. In this situation, one might question whether it is possible at all to obtain a permanent magnet material that is superior to the currently available maximum performance.

To answer this, one should have a perspective on the possible maximum performance of permanent magnet materials. One of way to do this is to estimate the upper limits of magnetization J_S, Curie temperature T_C, and lowest order uniaxial magnetic anisotropy constant K_1, which make a prospect about the performance of magnets. We discuss each of these quantities on the basis of the results obtained through first-principles calculation.

The discussions are based on all-electron electronic structure calculations performed within the local density approximation (LDA/GGA) of density functional theory (DFT). Machikaneyama (AkaiKKR) KKR-CPA package [1] was used, and for the calculation of T_C, Liechtenstein's method [2] was employed.

Figure 1 shows the calculated magnetization J_S of $3d$ elements as a function of the lattice constant a and atomic number Z. The fractional atomic number of a fictitious atom is used. The number of total electrons per atom is equal to Z. The crystal structure is assumed bcc. A prominent feature is that it has a dome-like structure appearing around $a = 2.65$ A and z=26.4, where J_S takes the maximum value of 2.66 T. It is pointed out that this is related to the fact that in the bcc structure, the interatomic distance between nearest neighbor pairs becomes small, forming a considerable bonding–antibonding splitting with a pseudo gap in between. Unfortunately, the lattice constant $a = 2.65$ A is 7 % too small compared with the equilibrium lattice constant of bcc Fe. Contrary to the general behavior of the magnetic moment that increases as the volume increases, the magnetic polarization increases with decreasing a up to some point where the magnetic state collapses.

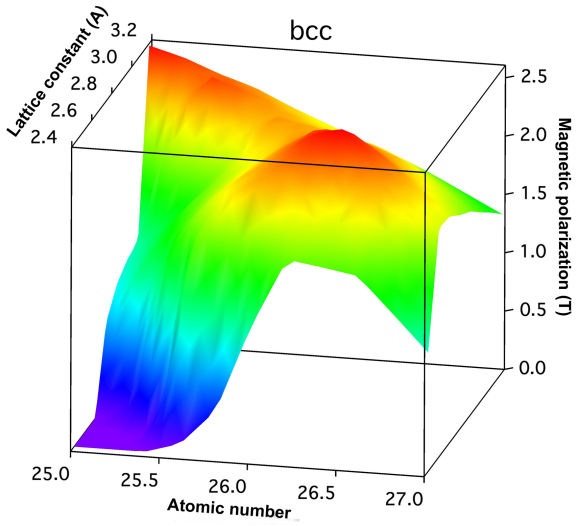

Figure 1: Saturation magnetic polarization J_S of the system plotted against the lattice constant and the fictitious atomic number[3].

Magnetic polarization takes on a large value at one of the corner points in the Z-a plane,

$Z = 25$ and $a = 3.2$ A, but this is not real. In this region, the antiferromagnetic state is more stable than the ferromagnetic state. Combining this fact with the information given by Fig. 1, we may conclude that a large J_S is expected only in the vicinity of the dome-like structure, and the upper limit of J_S would not exceed ~ 2.7 T.

Figure 2 shows the behavior of magnetic transition temperature T_C as a function of Z and a. Here, we again see a dome-like structure near $Z = 26.5$ and $a = 2.9$ A. This position approximately coincides with the position of the similar dome-like structure in J_S. This indicates that if $Z = 26.5$ and $a = 2.9$ A is forced by crystal structure, chemical composition, pressure, temperature, etc., $J_S \sim 2.7$ T is achieved. T_C drops rapidly toward the corner in the Z-a plane, $Z = 25$ and $a = 3.2$ A, where T_C becomes negative, meaning that the antiferromagnetic state should be the ground state. Now, we may say that the upper limit of T_C is ~ 2000 K (if fcc structure were assumed, the upper limit would be ~ 1500 K).

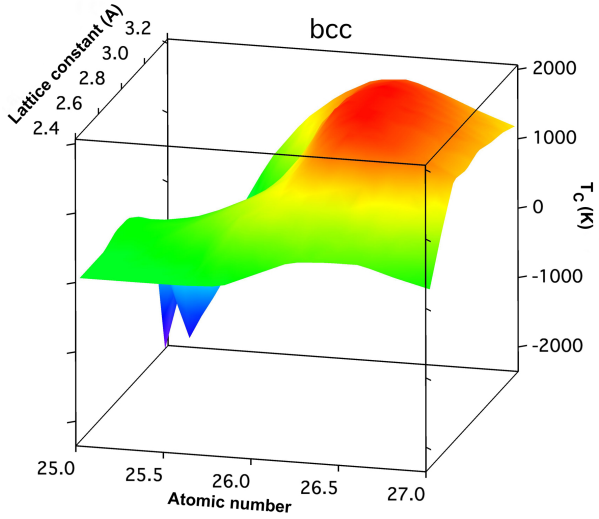

Figure 2: Magnetic transition temperature T_C of the system plotted against the lattice constant and the fictitious atomic number[3].

The main origin of magnetocrystalline anisotropy is spin orbit coupling. For Sm (Sm^{3+} in Sm-type Sm element), assuming that the orbitals are firmly bound to the lattice, the upper limit of the magnetic anisotropy constant K_1 estimated from the strength of the spin-orbit coupling , together with the values of $\langle L \rangle$, is as high as ~ 1000 MJm^{-3}. The upper limit of K_1 for other lanthanides, if scaled by the value of L, also would be similar to that of Sm. However, K_1 of rare earth magnetic materials is one to three orders of magnitude smaller than this values. This is because the anisotropy in lattice geometry is not large enough to firmly bind the orbital to the lattice: the $4f$ electron density rotates in line with magnetization to some extent. Therefore, the upper limit of K_1 is bound by the lattice geometry. Also, the magnetic moment carried by $3d$ orbitals of transition metal ions is only weakly coupled to the $4f$ orbitals of rare earth ions (through $3d$–$5d$ indirect and $5d$–$4f$ direct exchange coupling), the latter producing a large magnetic anisotropy. Accordingly, the magnetization is rather loosely bound to the lattice. The effect is in particular prominent at high temperature $T \gtrsim (2/3)T_C$, where the coupling between $3d$ and $4f$ becomes progressively weaker because of the thermal fluctuation.

In conclusion, calculations based on density functional theory conclude that the plausible upper limits of saturation magnetic polarization, magnetic transition temperature, and the magnetocrystalline anisotropy constant of permanent magnet materials could be $\sim$2.7 T, $\sim$2000 K, and $\sim$1000 MJm^{-3}.

References

[1] H. Akai, AkaiKKR, `http://kkr.issp.u-tokyo.ac.jp/` (2002).

[2] A. I. Liechtenstein, M. Katsnelson, V. Antropov, V. Gubanov, J. Magn. Magn. Mater. 67 (1987) 65.

[3] H. Akai: Scripta Materialia (2018), in press.