First principles calculations of magneto-crystalline anisotropy of rare-earth magnets

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Abstract
Magneto-crystalline anisotropies, $K_u$ and anisotropic magnetic fields, $H_{in}$ of two rare-earth (RE) magnets, i.e. CeFe$_{12}$ and PrFe$_{12}$, are theoretically calculated by using the crystal field (CF) method based on the first principles density functional theory (DFT) and the non-collinear DFT + U (NCDFT + U) method. The CF method reproduces an experimental $H_u$ of PrFe$_{12}$ but it failed to reproduce the $H_a$ of CeFe$_{12}$, providing $H_a$ with a wrong sign. The NCDFT + U method correctly reproduces experimental $H_a$ of CeFe$_{12}$ and PrFe$_{12}$, however the optimization of effective Hubbard onsite interaction parameters, $U_{eff}$, of the 4f electrons of the magnets is indispensable for the accurate calculation of $H_a$. We have found that the CF method is valid in so far as it is used for the study of $K_u$ of RE magnets, which have RE atoms heavier than Pr atom. We expect that the NCDFT + U method would become a quantitative $K_u$ calculation method of any RE magnets if the $U_{eff}$ calculation method of 4f electrons of RE magnets is established.

RE magnets as represented by Nd$_2$Fe$_{14}$B have attracted much attention in industry, because they exhibit a strong magnetization and can be used for several electro-magnetic apparatus such as high efficient electronic motors and generators [1, 2]. Another important physical property of magnets in addition to their magnetization strength is their coercivity [2], which indicates the strength of the magnets to keep their easy axis magnetization under a demagnetization field. Since magnets are usually used under a demagnetization field, knowing their coercivity is a subject of special importance in the study of magnets. The magnetization strength of a magnet can be theoretically calculated from first principles by making the electronic structure calculation of the magnet by using the spin–polarized DFT under the local spin density approximation (LSDA). The magnetization strength of a magnet is obtained from the difference of the up and down spin electron numbers, which are calculated by the spin-polarized DFT. On the other hand, there is no definitive theory capable of calculating the coercivities of magnets, as the mechanism of coercivity has remained unclear. Several mechanisms of coercivity are advocated [3], however it is certain that the coercivity of a magnet is closely related to its magneto-crystalline anisotropy, $K_u$ [2–4]. The $K_u$ of a magnet indicates the stability of its easy axis magnetization relative to its difficult axis magnetization, and can be calculated from first principles by investigating its electronic structure, taking into account the spin–orbit interaction (SOI). The $K_u$ of RE magnets are conventionally calculated by using the CF method [5–7]. The CF method assumes that RE magnets have strongly correlated 4f electrons localized at the RE atoms of the magnets, dehybridized from the itinerant electrons of the magnets, and calculates the $K_u$ of the 4f electron magnetization by investigating the dependence of the interaction energy of the 4f electron and CF of the magnets on the magnetization direction. The CF method has been thought to be valid for RE magnets, which should have strongly correlated electronic structures, but it has not been theoretically validated from first principles. Recently, in the community of first principles calculations, the non-collinear DFT (NCDFT) method has been emerging as a new theoretical tool of calculating $K_u$ of magnets [8]. The NCDFT method does not make any assumptions on the electronic structure of magnets, and calculates the $K_u$ of the magnets, investigating the magnetization dependent electronic structure, directly taking into account the SOI. By combining the DFT + U [9] and NCDFT methods, NCDFT + U method can be used for the $K_u$ calculation of RE magnets having
The crystal structures of CeFe₁₂ and PrFe₁₂ are energy-optimized, considering the correlation of 4f electrons of the Ce and Pr atoms of the magnets. The spin-polarized DFT calculation of CeFe₁₂. The NCDFT calculation is listed in Table 1 for the 4f electrons of which is larger than 3 eV.

The CF method has been applied to the Kₐ calculation of CeFe₁₂ and PrFe₁₂. A standard scheme of the CF method is used. The 4f electron orbitals of Ce and Pr atoms in the isolated Ce⁺³ and Pr⁺³ states are calculated by using the DFT method in the GGA, and the effective potentials, uₐ, of these RE magnets are obtained from their electronic structures calculated by using the GGA pseudopotential (PP) method using ultra-soft (US) PPs for Ce, Pr, Fe atoms. We used USPPs for Pr and Fe atoms, which have the 4f electrons of these atoms in the core state, to exclude the contribution of the 4f electrons to uₐ [13]. The uₐ are calculated as uₐ = V₁₉ + V₄₈ + V₁₆, where V₁₉ is the sum of the local potentials of PPs, V₄₈ is the Hartree potential, and V₁₆ is the exchange-correlation potential. We neglect the contribution of the non-local potentials of PPs to the uₐ because these potentials are short ranged and decays rapidly in the inter-atomic region. The CF parameters ⟨r⁴⟩Aₙm are obtained by expanding V eff at RE atom by real spherical harmonics Zₙm as [5],

\[
V_{\text{eff}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} A_{lm} \frac{(r^4)}{r} Z_{lm}(r).
\]

Here, \(r^4 = \int r^4 \varphi^2(r) dr\), and \(\varphi(r)\) is the radial part of the 4f electron orbital of Ce or Pr atom. CF parameters, and \(F_{lm}\) are numerical factors calculated by formulas given in [13]. \(\langle r^4 \rangle A_{20b}\), are calculated for the Ce and Pr atoms of CeFe₁₂ and PrFe₁₂, from the 4f electron orbitals for isolated Ce and Pr atoms in the isolated Ce⁺³ and Pr⁺³ states, and the \(u_{\text{eff}}\) of these RE magnets by using equation (1). The \(K_a\) of the magnets are calculated as [5],

\[
K_a = -3f(1/2)\alpha_j r^2 A_{20b} n_R,
\]

where \(f\) is total angular momentum and \(\alpha\) is the Stevens factor for the RE atom, which characterize the asphericity of the 4f electron density, and \(n_R\) is the number density of the atom. The SOI is implicitly taken into account in the assumption of the CF method that the 4f electron orbitals of RE atoms of a magnet rotates under an external magnetic field without changing their shape, conserving the total angular J = L + S, where L and S are the orbital and electron spin angular momentum quantum numbers, respectively. The dependence of A_{20b} on the orientation of the 4f electrons [5] is neglected. The Stevens factor used for the calculation is listed in Table 1 [14]. We used VASP for the electronic structure and \(V_{\text{eff}}\) calculations. The 4f electron orbitals \(\varphi(r)\) s of Ce and Pr atoms are calculated, using an atomic electronic structure calculation program GAO (Code for Investigating Atomic Orbitals) [15]. The \(r^4 A_{lm}\) s and \(K_a\) of the magnets were calculated by an electronic structure calculation program PATIO (Portable Ab initio Tools for Investigating Objects) [16].

The spin-polarized NCDFT + U PAW method under the GGA (NCGGA + U PAW) is used for the \(K_a\) calculations of CeFe₁₂ and PrFe₁₂. The \(K_a\) of these magnets are calculated, using a k-point set generated by

| RE ion | f | L | S | N | \(\alpha_f\) |
|--------|---|---|---|---|---------|
| Ce⁺³   | 5/2 | 3 | 1/2 | 1 | \[\frac{-2r_5^2}{5^2} \approx -5.714 \times 10^{-2}\] |
| Pr⁺³   | 4  | 5 | 1  | 2 | \[\frac{-2r_5^2}{5^2} \approx -5.714 \times 10^{-2}\] |
electric field.

Table 2. Magneto–crystalline anisotropies, \(K_s\) and \(H_s\), of CeFe\(_{12}\) and PrFe\(_{12}\), calculated by the crystal field (CF) theory and non-collinear DFT + U method in the generalized gradient approximation (NCGGA + U). Experimental \(H_s\) are shown for comparison.

|          | CF Theory | NCGGA + U | Exp. |
|----------|-----------|-----------|------|
|          | \(K_s\) (MJ m\(^{-3}\)) | \(H_s\) (T) | \(U_{\text{eff}}\) (eV) | \(K_s\) (MJ m\(^{-3}\)) | \(H_s\) (T) | \(H_s\) (T) |
| CeFe\(_{12}\) | –18.1 | –20.2 | 0 | 1.14 | 1.60 | 3.5 |
| PrFe\(_{12}\) | –6.9 | –7.6 | 0 | –10.13 | –15.25 | –5.97 |

For the calculation, the values of \(U_{\text{eff}}\) are obtained by using a plane wave cut-off of 500 eV. The calculations are conducted by changing the value of \(U_{\text{eff}}\) for the 4f electrons from 0.0 to 6.0 eV. Optimal \(U_{\text{eff}}\) most well reproducing experimental \(H_s\) for these magnets are found.

The NCGGA + U PAW calculations are conducted by using VASP.

Table 2 lists theoretical \(K_s\) and \(H_s\) of CeFe\(_{12}\) and PrFe\(_{12}\), calculated by the CF and NCGGA + U PAW calculations, along with experimental \(H_s\) for CeFe\(_{12}\) and PrFe\(_{12}\) [17, 18], for comparison. The theoretical \(H_{\text{us}}\) are obtained from the calculated \(K_s\) by using the relation \(H_{\text{us}} = 2K_s/M_s\), where \(M_s\) is saturation magnetization. Here, the \(H_s\) and \(K_s\) results by the CF method include the contribution from itinerant Fe\(^{3d}\) electrons of the magnets, which are calculated by the NCGGA PP method. The contribution is calculated by using PPs for Ce and Pr atoms, which have 4f electrons in the core state.

The negative \(H_s\) and \(K_s\) indicate that the easy axis of magnetization of the magnets is in their \(ab\) plane and the positive \(H_s\) and \(K_s\) indicate that the easy axis is parallel to their \(c\) axis. The CF results for CeFe\(_{12}\) provide a negative \(H_{\text{us}}\) contrary to an experiment, which gave a positive \(H_{\text{us}}\) for the magnet. The results indicate that the CF method is inadequate for the CeFe\(_{12}\) calculation of CeFe\(_{12}\). Ce\(^{3+}\) ions are known to exhibit the valence fluctuation [19, 20] between Ce\(^{3+}\) and Ce\(^{4+}\), and the correlation of the 4f electron of the ions is weak, having an intermediate nature between itinerant and correlated electrons. Thus, the failure of the CF method is understood to be due to the valence fluctuation of the Ce atoms of CeFe\(_{12}\), which lowers the strong correlation of the 4f electrons of the atoms. The CF calculation gives a negative \(H_s\) for PrFe\(_{12}\), agreeing with an experimental fact that the \(H_s\) of PrFe\(_{12}\) is negative, though the calculation overestimated the \(H_s\) strength by about 27%. The CF results of PrFe\(_{12}\) indicate that the assumption of the CF method—the rare-earth magnet should have strongly correlated 4f electrons and the electrons are dehybridized from itinerant electrons—rather hold in the PrFe\(_{12}\) case. However, the overestimation of the strength of \(H_s\) of PrFe\(_{12}\) suggests that the assumption is too simple and that there are some hybridizations between the correlated 4f and itinerant electrons of the magnet.

Table 2 shows that the CF result at this \(U_{\text{eff}}\) value is unstable at \(U_{\text{eff}} = 1\) eV, and we omitted the calculation result at this \(U_{\text{eff}}\) value.

Monkhorst-Pack scheme of (10 \times 10 \times 10), which has 1000 \(k\)-points in the Brillouin zone (the calculation is performed in the \(P_1\) symmetry). We use unit cells containing 13 atoms. The energies of the magnets are calculated by setting its magnetization to the [100], [010], [001] directions, and their easy and difficult axes of magnetization are found. The \(K_s\) of CeFe\(_{12}\) is obtained from the energy differences of CeFe\(_{12}\) magnetized in the easy axis and that magnetized in the difficult axis. The \(K_s\) of PrFe\(_{12}\) is similarly obtained. The calculations are conducted, using a plane wave cut-off of 500 eV. The calculations are conducted by changing the \(U_{\text{eff}}\) for the 4f electrons from 0.0 to 6.0 eV. Optimal \(U_{\text{eff}}\) most well reproducing experimental \(H_s\) for these magnets are found.
those of PrFe$_{12}$ between 3.3 and 3.4 eV. That is, the changes of $K_u$ and $H_a$ of PrFe$_{12}$ are more abrupt. These changes of $K_u$ and $H_a$ of CeFe$_{12}$ and PrFe$_{12}$ indicate that these RE magnets change their electronic structure from itinerant to strongly correlated at $U_{\text{eff}}$ of about 3 eV. From this understanding and the optimal $U_{\text{eff}}$ for CeFe$_{12}$ and PrFe$_{12}$, it is assumed that CeFe$_{12}$ has an itinerant electronic structure and PrFe$_{12}$ has a strongly correlated electronic structure. This understanding accorded with the ideas for the electronic structure of CeFe$_{12}$ and PrFe$_{12}$, obtained from the CF results. Thus, the CF method is suggested to be valid for the $K_u$ calculation of RE magnets, the $U_{\text{eff}}$ for the $4f$ electrons of which is over 3 eV, having strongly correlated electronic structures. The RE atoms heavier then Pr are smaller than Pr atom because of the lanthanide contraction and have more localized $4f$ orbitals than Pr atom. The $U_{\text{eff}}$ for localized electrons generally increases as the degree of the localization becomes larger. The $U_{\text{eff}}$ for $4f$ electrons of RE magnets having RE atoms heavier than Pr should be larger than 3 eV so the CF method is considered to have a sound physical basis in so far as it is applied to the $K_u$ calculation of such magnets. However, one should keep in mind that the method tends to overestimate the strength of $K_u$, because it neglects the hybridization of correlated $4f$ and itinerant electrons of RE magnets. The optimal $U_{\text{eff}}$ for the NCDFT + U method of CeFe$_{12}$ and PrFe$_{12}$ are substantially smaller than empirical $U_{\text{eff}}$ values for $4f$ electrons of Ce and Pr atoms, which are 5 and 6 eV, respectively [19, 20]. The smallness of the optimal $U_{\text{eff}}$ for the $4f$ electrons of CeFe$_{12}$ and PrFe$_{12}$ indicates that the on-site interactions between the $4f$ electrons are substantially reduced by the interaction screening by the itinerant Fe $3d$ electrons of the magnets. This means that empirical $U_{\text{eff}}$ for $4f$ electrons of RE atoms are useless for the accurate $K_u$ calculation of RE magnets by the NCGGA + U method. For the $a$ priori prediction of $K_u$ of RE magnets, theoretical calculations of $U_{\text{eff}}$ of their $4f$ electrons is necessary and is the subject of future study. The self-consistent constraint DFT (scsDFT) technique recently developed by Hamada and Ohno [21] is thought to be effective for this purpose.

In conclusion, we have found that the CF method is valid in so far as it is used for the $K_u$ calculation of most RE magnets having RE atoms heavier than Pr atom. However, because of its simple assumption on RE magnet electronic structure, the calculation accuracy of the CF method is rather low as demonstrated by the PrFe$_{12}$ calculation of this study. To calculate the $K_u$ of a RE magnet, quantitatively, we need to determine the $U_{\text{eff}}$ for $4f$ electrons of the magnet and make NCGGA + U calculations of the magnet. The $U_{\text{eff}}$ calculation method of $4f$ electrons of RE magnets has not been established yet but there are some important progresses in this field, such as the constrained random phase approximation [22] and scsDFT technique. If the $U_{\text{eff}}$ calculation method of $4f$ electrons of RE magnets is established, the NCGGA + U method would become an accurate $K_u$ calculation method of the magnets.

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