Effect of lattice relaxation on magnetic anisotropy: Zr-doped Sm_2Co_{17}

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The magnetic anisotropy energy (MAE) in rare-earth/transition-metal hard magnets originates from the onsite anisotropy of the rare-earth element with additional contribution from the transition-metal sublattice. While $SmCo_5$ can be transformed to Sm_2Co_{17} by partial substitution of Sm by Co_2 dumbbells, the MAE in Sm_2Co_{17} is noticeably smaller compared to that in $SmCo_5$. However, small dopings of nonmagnetic Zr significantly increase the MAE in Sm_2Co_{17}. We show that the changes to the MAE in Sm_2Co_{17} can be traced down to the reduction of the crystal field at the Sm site due to the Co sublattice relaxation upon $Sm \rightarrow Co_2$ substitution which is subsequently restored upon substitution of $Co_2 \rightarrow Zr$.

The magnetic anisotropy energy (MAE), the difference between the ground-state energies due to rotation of the magnetization direction, is one of the most elusive electronic properties. Not only is it very difficult to compute, being a small difference of very large numbers, but also it often includes comparable contributions from different physical origins. Even in the elementary metals the physics of the MAE is not well understood.[1] Paradoxically, the MAE of more complicated hard magnets, such as Sm-Co compounds, is often easier to rationalize. In particular, we have proposed a consistent physical picture of MAE in YCo_5 (Ref. 2) and $SmCo_5$ (Ref. 3) based on first-principles calculations. However, Sm_2Co_{17}, although technologically more important, is less well understood. Indeed, despite crystallographic similarities, the MAE of Sm_2Co_{17} (Ref. 4) is much smaller than that of $SmCo_5$ (Refs. 5–8), 3.6×10^6 J/m^3 compared to 26×10^6 J/m^3, respectively, corresponding to 5.0 meV/Sm compared to 16 meV/Sm. On the other hand, the MAE can be substantially (by a factor of two) enhanced with one Zr per 19 atom unit cell.[9,10] It seems, at first glance, extremely puzzling how such a small doping can so greatly change an electronic property which is mostly associated with the quasiatomic $4f$ shell of the Sm atom. Indeed, doping with up to ~30% Fe, a magnetic element, leads to only modest increases in the MAE.[11] Zr does not change the structure of the d band enough to directly contribute to this large increase of the MAE,[12] so the source must be changes to the crystal structure which have a subtle but profound impact on the MAE.

In this paper we show that the picture which explains the MAE in $SmCo_5$ (Ref. 3) can also explain both the reduced MAE in Sm_2Co_{17} and its giant increase with Zr doping. Both effects appear to be related to the changes in the crystal field on the Sm site.

First, we need to understand the crystallographic difference between the two compounds. The crystal structure of Sm_2Co_{17} is derived from that of $SmCo_5$ [Fig. 1(a)] by replacing every third Sm atom by a Co_2 dumbbell, oriented perpendicularly to the hexagonal plane. Figure 1(b) shows $\frac{2}{3}$ of the Sm_2Co_{17} unit cell, including one Sm and one CO_2 dumbbell. Note that the neck of the dumbbell appears in the former Sm-Co_2 plane, having a much smaller effective in-plane radius than the Sm ion for which it substitutes. Therefore, as one can see from Fig. 1(b), the surrounding hexagon

of Co ions relaxes towards the center point of the Co_2 dumbbell, so that the distance between this point and the surrounding Co's is only 2.38 Å, while the Co-Sm distance increases to 3.04 Å, compared to 2.89 Å in $SmCo_5$.[13] There is also a minor, unimportant warping of the Co planes resulting from the dumbbell ordering.

The MAE in Sm-Co compounds arises from the on-site magnetic anisotropy of the Sm $4f$ shell, which strongly depends on the crystal field, and, to a lesser extent, on the Co sublattice itself.[3] Qualitatively, the large MAE of Sm in $SmCo_5$ can be understood as follows: The spin-orbit interaction in the $4f$ shell favors Hund's 2nd rule ordering of the $4f$ states to maximize the projection of the orbital moment onto the magnetic-field direction. The deepest state has the orbital
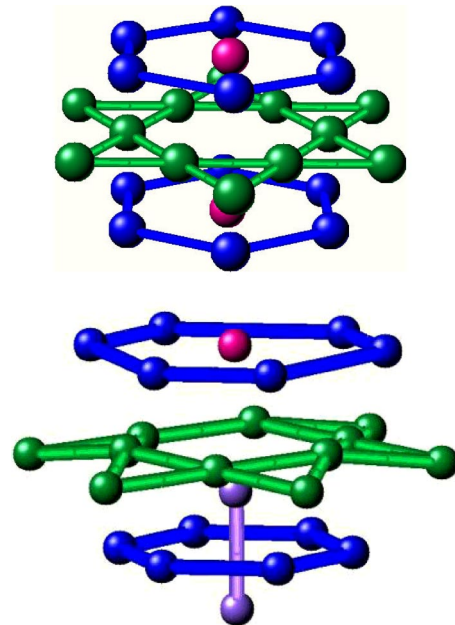

FIG. 1. (a) Crystal structure of $SmCo_5$. Sm (or Y) lies in the middle of the hexagonal Co(2c) layers, while the Co(3g) lattice forms a Kagome lattice in the XY plane. (b) Two-thirds of the crystal structure of Sm_2Co_{17}. One of the Sm atoms of the $SmCo_5$ crystal structure is replaced by a Co_2 dumbbell with distortions to the Co lattice. These distortions include an increase in the size of the Co ring around Sm and a reduction of the size of the Co ring around the Co_2 dumbbell.

moment $L=3$, the next one $L=2$, etc. If one neglects the crystal field entirely, according to atomic Hund's rules the whole $4f$ shell rotates with the field with no change in energy. However, if the crystal field is present, the energy of its interaction with the $4f$ shell contributes to the MAE, and this contribution gets larger with a stronger crystal field. On the other hand, if the spin-orbit interaction were much *smaller* than the crystal field, as in the case of Co, the orbital moment would have been quenched ($L\approx0$) and all $4f$ states would have included combinations of the spherical harmonics with both signs, $m=\pm3$, $m=\pm2$, etc. In this situation, when the magnetic field is rotated, the $4f$ shell does not rotate, making any interaction of its (small) orbital moment with the magnetic field the source of the MAE. Obviously, the optimal situation is when both interactions are of the same order of magnitude, producing $4f$ states which are neither pure spherical harmonics nor pure lattice (real) harmonics but a mixture of the two.

This exactly describes the situation in $SmCo_5$,[3] as illustrated in Fig. 2(a).[15] The peaks in the density of states correspond to the individual $4f$ states. The lowest energy peak is formed by the spherical harmonic with $m=3$, in accord with Hund's 2nd rule. The next peak is formed by the second and third "Hund" states with $m=2$ and $m=1$, but, contrary to the situation in a free ion, the distance between the two is practically zero. The remaining $4f$ states are mixtures of different spherical harmonics, intermediate between atomlike "pure-m" states and the lattice harmonic states. This is an indication that the two competing interactions, crystal-field and spin-orbit, are similar in strength, corresponding to the largest MAE among the Sm-Co compounds, 16 meV/f.u.[5−8] After subtracting the MAE of YCo_5, 4 meV/f.u.,[16] which we have shown corresponds to the MAE of the Co sublattice itself,[3] we find 12 meV/Sm for the Sm onsite MAE in $SmCo_5$.

Now we compare this with Sm_2Co_{17}. First of all, the MAE of Y_2Co_{17}, -1.6 meV/f.u,[17] has the opposite sign to that of YCo_5.[16] With the experimental MAE for Sm_2Co_{17}, ~10 meV/f.u.,[4] this gives 5.8 meV/Sm after subtracting off the Co contribution, substantially less than in $SmCo_5$. Indeed, when we compare the density of state plots for $SmCo_5$ [Fig. 2(a)] and for Sm_2Co_{17} [Fig. 2(b)], we observe that in Sm_2Co_{17} the $4f$ states, in terms of their width and their m ordering, much more closely resemble atomic orbitals. These $4f$ states are ordered by Hund's 2nd rule and are nearly pure spherical harmonic states, the only difference from the free atom being that the $4f$ levels are not equidistant. Since the spin orbit coupling is obviously the same in both compounds, we conclude that the crystal field in Sm_2Co_{17} is substantially weaker.

This fact can be traced down to different crystallography. The main contribution to the crystal field comes from d-f hybridization.[14] Using Harrison's canonical scaling,[18] we find that the d-f hopping amplitudes (t_{df}) should depend on the Sm-Co distance (D), approximately, as $D^{l+l'+1}=D^6$. The difference of 4% in the Sm-Co distance translates into a 25% difference in t_{df}. If we recall that in the limit of large separation between the Co $3d$ and the Sm $4f$ bands the crys-
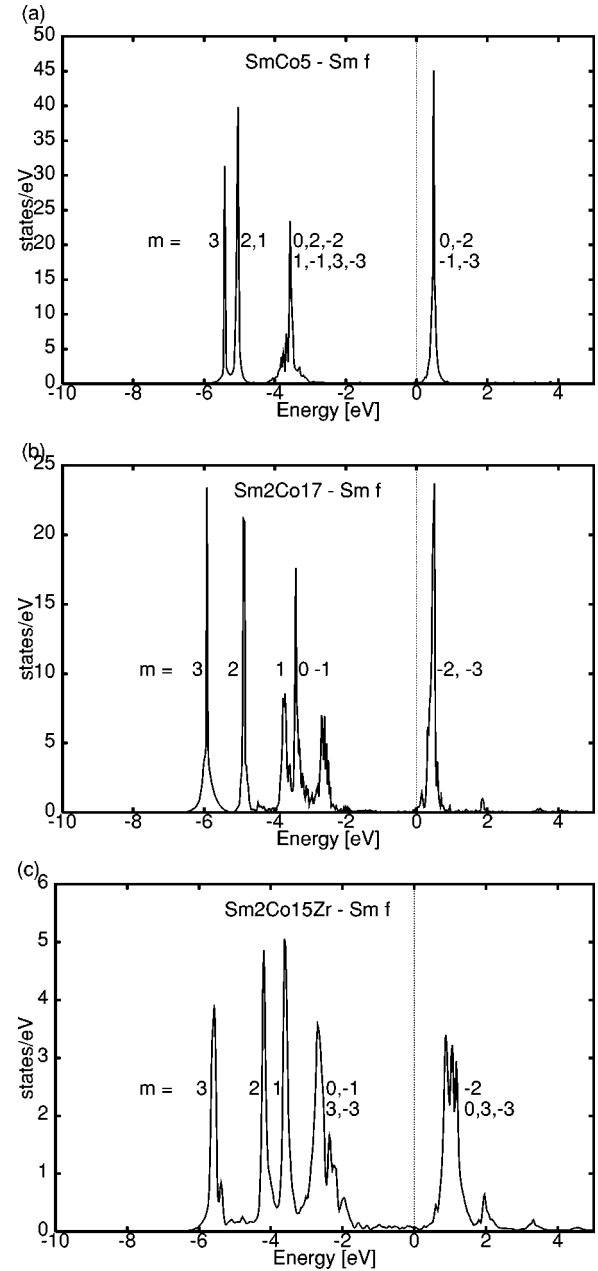

FIG. 2. The Sm $4f$ character of $SmCo_5$, Sm_2Co_{17}, and $Sm_2Co_{15}Zr$, all with relaxed lattice parameters and internal coordinates. Note the peaks of individual m character in Sm_2Co_{17} arising from weak crystal field effects. In $SmCo_5$ and $Sm_2Co_{15}Zr$ the peaks are combinations of real and lattice harmonics due to strong crystal-field and spin-orbit interactions, which are best for large MAE.

tal field is defined by the ratio $t_{df}^2/(\epsilon_d-\epsilon_f)$ (for band energies ϵ_d and ϵ_f), we see that up to 50% reduction of the crystal field in Sm_2Co_{17} may be expected for some $4f$ states compared to that in $SmCo_5$!

We shall now turn to the dramatic increase in the MAE observed in Sm_2Co_{17} upon Zr doping.[9,10] A variety of dopants used on Sm_2Co_{17}, including Fe, Mn, Cr, Cu, and Al, which dope the Co interlayer sites showed a small increase in the anisotropy,[11] but the large increase of the MAE was found for V, Ti, Zr, and Hf (Ref. 10) which dope either the

TABLE I. The atomic positions (rhombohedral coordinates) of Sm, Co_2 (dumbbell), and Zr as well as the Co atom lying closest to these atoms in Sm_2Co_{17} and $Sm_2Co_{15}Zr$ before and after relaxation. The nearest-neighbor Sm-Co, Co_2-Co, and Zr-Co distances are given in angstroms (Å), along with the Sm-Co nearest-neighbor distance in $SmCo_5$.

	Before relaxation	After relaxation
Sm_2Co_{17}		
Sm	0.343,0.343,0.343	0.359,0.359,0.359
Co	0.283,0,0.717	0.284,0,0.716
Co_2	0.099,0.099,0.099	0.0953,0.0953,0.0953
Sm-Co	3.04 Å	3.05 Å
Co_2-Co	2.37 Å	2.38 Å
$Sm_2Co_{15}Zr$		
Sm	0.343,0.343,0.343	0.331,0.331,0.331
Co	0.283,0,0.717	0.316,0,0.684
Zr	0,0,0	0,0,0
Sm-Co	3.04 Å	2.88 Å
Zr-Co	2.38 Å	2.65 Å
$SmCo_5$		
Sm-Co	2.89 Å	2.89 Å

Sm or the Co_2-dumbbell site due to their large atomic radii.[19] The dopant which has been found to produce the largest increase in the MAE is Zr (Refs. 9,10) where the MAE increases from $\sim$10 meV/f.u. to $\sim$20 meV/f.u. (or from 5.0 meV/Sm to 10 eV/Sm) (Ref. 9) with $\sim$6% Zr replacement for Co, which is approximately one Zr per unit cell.

Some controversy exists in the literature about where the Zr atoms go within the Sm_2Co_{17} crystal structure. Fujii et al.[9,10] and Rabenberg et al.[20] suggested that the Zr atoms replace the interlayer Co, but that would have led to a significant *increase* of both *a* and *c* parameters, which is not seen in their data.[9,10,20] Ray[21] pointed out that the large atomic radius of Zr would prevent this type of substitution but would probably favor substitution of the Co_2 dumbbell sites, though substitution for Sm was possible. Lefevre et al.[19] performed an x-ray analysis of Zr substitutions in Sm_2Co_{17} which found that $\sim$90% of the Zr goes into the Sm sites and $\sim$10% to the Co_2 dumbbell sites, which is consistent with the significant *decrease* of *a* and a small *increase* in *c* in his samples. However, the MAE for these samples were not measured. On the other hand, in previous studies[9,10,20] where the large increases in the MAE have been measured, an opposite trend has been observed, a significant *increase* in *a* and a small *decrease* in *c*. This strongly suggests that Zr in these studies substitutes mostly for the Co_2 dumbbells since the skinny, out-of-plane dumbbell is replaced by a sphere, unlike in Lefevre et al.'s[19] samples. As discussed below, since the Zr substitution of the Sm sites does not change the Sm-Co distance significantly, no increase in the MAE would be seen for this substitution. Preparation conditions may lead to differences in the observed Zr substitution. Our calculations assume Zr replacing the Co_2 dumbbells which we show leads to the large increase in the MAE.

The MAE of Sm_2Co_{17} is lower than that of $SmCo_5$ not only because the onsite MAE of Sm is reduced but also because the MAE of the Co sublattice changes sign. Although the effect of Zr on Y_2Co_{17} has not been measured, Ti and Mo, which like Zr dope on the Co_2 site, change the MAE direction from planar to uniaxial, from -1.6 meV/f.u. in Y_2Co_{17} to 2.2 meV/f.u.[17] for one Ti per formula unit. Subtracting off the latter number from the MAE of Sm_2Co_{17}+Zr,[9,10] the Sm contribution to the MAE increases from 5.8 meV/Sm in Sm_2Co_{17} to 8.9 meV/Sm upon a doping of one Zr per unit cell. We conclude that the main source of the MAE by Zr doping is due to the increase in the Sm MAE. Note that Zr doping does not increase the MAE in other Sm-Co materials. For instance, Zr doping in $SmCo_5$, where Zr prefers the Sm site, significantly reduces the MAE.[22]

Direct calculations of the MAE, as we had performed in YCo_5 (Ref. 2) and $SmCo_5$ (Ref. 3), would prove very difficult in Sm_2Co_{17} due to its much more complex crystal structure. However, it is feasible to investigate the differences in the electronic structure and crystal field due to changes to the crystal structure with Zr substitution for the Co_2 dumbbells. We began by performing full structural relaxation on both Sm_2Co_{17} and $Sm_2Co_{15}Zr$ (full Zr substitution for the Co_2 dumbbells in the unit cell) for the total volume, c/a ratio, and internal coordinates. The volume and c/a ratio changed by $\lesssim$2% from the experimental values for both materials. While all of the internal coordinates were allowed to change, the intermediate Co layer (which did not contain Sm, Zr, or the Co_2 dumbbells) showed changes in their positions by $\lesssim$2%. The relaxed positions of the Co in the same layer as Sm, Zr, or the Co_2 dumbbells, which show strong changes with Zr doping, are given in Table I along with the nearest-neighbor Sm-Co, Zr-Co, and Co_2 (dumbbell)-Co distances. The Sm-Co distance in $SmCo_5$ is given as a reference. The relaxed Sm-Co and Zr-Co nearest-neighbor distances are 2.87 and 2.65 Å, respectively. The latter number is 0.27 Å larger than the Sm-Co_2 dumbbell distance in Sm_2Co_{17},

meaning the neighboring Co's are pushed away from Zr and closer to the Sm ions. As a result Sm-Co distance becomes smaller, very close to that in $SmCo_5$.

We can now see the effect of this shortening of the Sm-Co distance on the crystal field on Sm [Fig. 2(c)]. As in $SmCo_5$, only the lowest peaks represent ''pure-m'' states. The other states are strong mixtures of spherical harmonics with different values of m, just as in $SmCo_5$, but very different from Sm_2Co_{17}. We see that the crystal field in $Sm_2Co_{15}Zr$ is similar in strength to that in $SmCo_5$ and considerably stronger than in Sm_2Co_{17}, consistent with the fact that the MAE of the Sm ions in Sm_2Co_{17} is closer to that in $SmCo_5$ and is much larger than that in Sm_2Co_{17}.

In conclusion, we present a theoretical picture of formation of the large magnetic anisotropy in Sm-Co magnets. By analyzing the structure of the $4f$ states, rendered by our first principles LDA$+U$ electronic structure calculations, we conclude that the weaker crystal field effects are responsible for a substantial reduction of magnetic anisotropy in Sm_2Co_{17}, as compared to $SmCo_5$. The restoration of the anisotropy upon small doping with Zr is due to lattice relaxation around the Zr atom, which we have calculated directly, and found it sufficient to restore the crystal field on the neighboring Sm to nearly its $SmCo_5$ value.

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[14] Contrary to popular belief, it is d-f hybridization that yields most of the crystal field (CF). This can be verified within the linear muffin-tin orbital (LMTO) method, where d-f hybridization can be turned off, which reduces the CF splittings by a factor of 5. One can also estimate the ''standard'' Coulomb CF, using calculated ionic charges, and this estimate is much smaller than that actually found. Note that the Coulomb CF also strongly depends on the Sm-Co distance, as D^{-2}, albeit not as strongly as the hybridization-induced CF.

[15] All calculations presented in this paper were performed using the linear augmented plane wave method (Ref. 23) implemented in the WIEN2K code (Ref. 24). LDA$+U$ correction was used for Sm f orbitals. The details of the calculations are described in our previous papers (Refs. 2, 3, and 12).

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