

9-20-2004

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Sabirianov, Renat F.; Kashyap, Arti; Skomski, Ralph; Jaswal, Sitaram; and Sellmyer, David J., "First principles study of transition-metal substitutions in Sm–Co permanent magnets" (2004). *David Sellmyer Publications*. 28.

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First principles study of transition-metal substitutions in Sm–Co permanent magnets

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(Received 6 January 2004; accepted 23 July 2004)

The microchemistry and magnetism of conventional and high-temperature Sm–Co permanent magnets are investigated by first-principles calculations. Particular emphasis is on the site preference for the substitution of Cu, Ti, and Zr in SmCo₅ and Sm₂Co₁₇ compounds. Cu substitution is more favorable in the 1:5 phase, in agreement with experimental findings. Titanium and zirconium have positive solution energies for both the phases, with Ti(Zr) having slight preference for the 1:5 (2:17) phase. Some Zr may segregate to the phase boundaries because of its large solution energy. For Ti and Zr the dumbbell site of the 2:17 phase is preferred over the other three inequivalent cobalt sites. These results are used to discuss the observed cellular nanostructure of the high-temperature Sm–Co hard magnets with composition close to the 2:17 phase. © 2004 American Institute of Physics. [DOI: 10.1063/1.1792791]

Since the development of the first samarium–cobalt magnets in the 1970s, materials based on SmCo₅ and Sm₂Co₁₇ (see Table I for their basic magnetic properties) have become an important class of permanent magnets.^{1–3} In particular, they continue to be used in applications well above room temperature, where they are superior to other high-performance rare-earth magnets, such as Nd₂Fe₁₄B.^{4–10} The high coercivity of samarium–cobalt magnets originates from the Sm sublattice anisotropy, whereas the Co sublattice yields a high Curie temperature and stabilizes, via intersublattice exchange, the magnetic anisotropy at high temperatures.¹¹ A common feature of both room-temperature and high-temperature Sm–Co magnets is the use of additives such as Cu, Zr, and Ti, which yield a two-phase structure where a 1:5 type grain-boundary phase surrounds 2:17 type main-phase cells.

The two-phase nanostructure is necessary to obtain coercivity at zero and finite temperatures, by realizing domain-wall pinning at the 1:5 grain-boundary phase. The Cu, which exhibits a high solubility in the 1:5 phase, essentially contributes to the phase segregation and tunes the anisotropy of the grain-boundary phase.⁵ The latter effect is strongly temperature dependent,⁴ because the reduction of the anisotropy of the grain-boundary phase due to Cu is particularly pronounced at high temperatures. While Cu seems to be necessary in any two-phase Sm–Co magnet, Zr, Ti, and some other elements can replace each other, although both the microstructure and the magnetic properties are affected by the choice.^{4–8} At room temperature, optimized Zr-containing magnets are superior to Ti-containing magnets, but this is no longer true for magnets whose composition and heat treatment are chosen to optimize the coercivity at temperatures of the order of 500 °C.⁴ This and the somewhat different micro-

structures of Zr- and Ti-containing magnets¹² indicate differences in the site-specific occupancies by the additives. This affects the intra- and intersublattice exchange interactions, the Curie temperature,¹³ and—indirectly¹¹—the finite-temperature anisotropy and coercivity.

So far there are no first-principles calculations of the solubility of additives in the SmCo₅ and Sm₂Co₁₇ phases. This refers not only to the more recently considered high-temperature magnets, but also to conventional room-temperature Sm–Co permanent magnets. A relatively good phenomenological description of the phase structure has been achieved, but a thorough theoretical understanding and further optimizations and improvements of the magnets requires a first-principles analysis of the solution energies and energy differences. In this letter, we report first-principles calculations of the solubilities of Cu, Ti, and Zr in SmCo₅ and Sm₂Co₁₇. We use the Vienna *ab initio* simulation package (VASP)^{14,15} to study the phase preference by these impurities and their effects on the magnetic moments.

There is a generic connection between 1:5 and 2:17 phases. Sm₂Co₁₇ can be obtained from SmCo₅ by appropriate substitution of the Sm atoms with a pair of Co atoms called dumbbell pair.³ The number of inequivalent cobalt sites increases from two for SmCo₅ to six for Sm₂Co₁₇. The presence of the dumbbell pair in 2:17 phase creates additional elastic stresses in the system, which results in increasing the

TABLE I. Saturation magnetization (in T), Curie temperature (in K), and anisotropy constant (in MJ/m³).

Compound	$\mu_0 M_s$	T_C	K_1
SmCo ₅	1.07	1020	17
Sm ₂ Co ₁₇	1.22	1190	3.3

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TABLE II. The energies (in eV/supercell) and magnetic moments (in μ_B /supercell) of supercells of SmCo_5 and $\text{Sm}_2\text{Co}_{17}$ with and without impurities.

Compound	Energy	Magnetic moments
SmCo_5	-479.335	79.88
SmCu_5	-285.239	
SmTi_5	-433.965	
SmZr_5	-299.771	
ZrCo_5	-594.950	76.27
Cu in c site of SmCo_5	-476.985	78.75
Cu in g site of SmCo_5	-477.024	79.91
Ti in c site of SmCo_5	-481.600	77.90
Ti in g site of SmCo_5	-481.064	76.94
Zr in c site of SmCo_5	-480.973	75.96
Zr in g site of SmCo_5	-481.081	76.45
Zr in RE site of SmCo_5	-483.544	78.67
$\text{Sm}_2\text{Co}_{17}$	-388.035	74.68
$\text{Sm}_2\text{Cu}_{17}$	-220.194	
SmTi_{17}	-352.128	
SmZr_{17}	-222.555	
$\text{Zr}_2\text{Co}_{17}$	-475.605	62.79
Cu in c site of $\text{Sm}_2\text{Co}_{17}$	-384.610	72.94
Cu in d site of $\text{Sm}_2\text{Co}_{17}$	-384.457	72.91
Cu in f site of $\text{Sm}_2\text{Co}_{17}$	-384.619	72.84
Cu in h site of $\text{Sm}_2\text{Co}_{17}$	-384.745	72.85
Ti in c site of $\text{Sm}_2\text{Co}_{17}$	-389.911	70.39
Ti in d site of $\text{Sm}_2\text{Co}_{17}$	-388.987	70.60
Ti in f site of $\text{Sm}_2\text{Co}_{17}$	-389.284	70.03
Ti in h site of $\text{Sm}_2\text{Co}_{17}$	-389.013	70.69
Zr in c site of $\text{Sm}_2\text{Co}_{17}$	-389.938	70.27
Zr in d site of $\text{Sm}_2\text{Co}_{17}$	-388.286	70.41
Zr in f site of $\text{Sm}_2\text{Co}_{17}$	-389.046	69.71
Zr in h site of $\text{Sm}_2\text{Co}_{17}$	-388.778	70.62
Zr in RE site of $\text{Sm}_2\text{Co}_{17}$	-392.187	73.87

c axis while reducing the *a*-axis lattice parameter. Since the compounds being studied here are close-packed, the transition-metal impurities are expected to substitute for Co. Due to the comparatively big size of the Zr atom, we have also checked the possibility of its substitution for the rare-earth site.

In order to study the phase preference of the impurities we calculate the total energy of the supercell that contains one impurity atom. We have chosen a supercell of 72 atoms for SmCo_5 , corresponding to $2 \times 2 \times 3$ unit cells with 6 atoms per unit cell, and a supercell of 57 atoms for $\text{Sm}_2\text{Co}_{17}$, corresponding to three formula units. We use a relatively small number of *k* points with $4 \times 4 \times 2$ division of the Brillouin zone because of the large size of the super cell. The positions of the atoms were relaxed using the VASP program, in order to obtain accurate solution energies. Impurities of Cu, Ti, and Zr were considered at each inequivalent position of the Co sites, and the energies of the basis compounds were calculated as well. Table II shows the results of these calculations.

The relative stability of an impurity in the two phases was inferred from these calculations. Using the results in Table II we have calculated the impurity solution energies. For example, for a Cu impurity in SmCo_5 , the solution energy is given by

TABLE III. The solution energies (in eV) of various impurities in SmCo_5 and $\text{Sm}_2\text{Co}_{17}$.

SmCo_5	E_{solution}	$\text{Sm}_2\text{Co}_{17}$	E_{solution}
Cu(c)	-2.895	Cu(c)	0.480
Cu(g)	-0.386	Cu(d)	0.633
		Cu(f)	0.471
		Cu(h)	0.345
Ti(c)	-0.346	Ti(c)	-2.506
Ti(g)	-2.359	Ti(d)	-1.582
		Ti(f)	-1.879
		Ti(h)	-1.608
Zr(c)	-4.132	Zr(c)	-4.806
Zr(g)	-4.240	Zr(d)	-3.154
Zr(RE)	-2.166	Zr(f)	-3.914
		Zr(h)	-3.646
		Zr(RE)	-2.616

$$E_{\text{sol}} = E[(\text{SmCo}_{5-1/N}\text{Cu}_{1/N})_N] - \frac{6N-1}{6N}E[(\text{SmCo}_5)_N] - \frac{1}{6N}E[(\text{SmCu}_5)_N],$$

where E represents the energy of the supercell having N formula units. (In the present calculations, $N=12$ for 1:5 compounds and $N=3$ for 2:17 compounds). Solution energies computed using the above relation are given in Table III. A negative (positive) value of E_{sol} implies that the impurity is soluble (insoluble) in the host.

Table III shows that Cu is soluble in 1:5 but not in 2:17, in agreement with experiment.¹⁶ This is responsible for the two-phase mixture when a Sm-Co system with composition close to 2:17 is doped with Cu. We also see from the results in Table III that Ti can go into either phase, with a slight preference for the 1:5 phase. By comparison, Zr can go to either phase with a preference for the 2:17 phase. While Ti and Zr doping have similar effects on the Sm-Co system, the slight preference of the Zr for the 2:17 phase may explain the relatively easy formation of the hexagonal 2:17 platelet phase, which has been associated with the presence of Zr.^{2,3} In fact, the main structural difference between Zr, and Ti-doped 2:17 type magnets is the presence of a lamellar phase in the case of Zr and its absence in the case of Ti.¹²

In the 2:17 phase, the dumbbell site is the site preferred for substitution by both Ti and Zr. We have also examined the possibility that Zr replaces Sm, as suggested by the similar sizes of the elements. The solution energy results in Table III show that Zr overwhelmingly prefers Co sites over the Sm sites in both compounds. The calculated magnetic moments for Ti and Zr-substituted compounds are close to the experimental findings.

Our calculations support the following qualitative picture. The doping of Sm-Co system with Cu causes the formation of a SmCo_5 phase, whereas Zr and Ti are present in both phases helping to produce a microstructure suitable to create coexistence.¹⁷ These phases have mismatch of lattice parameters which depends on the doping concentration. This will create elastic stresses in the system. At some window of doping concentration the system creates a cellular microstructure which lowers energy by removing these stresses.

In conclusion, we have performed a detailed study of the relative phase stability of SmCo_5 and $\text{Sm}_2\text{Co}_{17}$ doped with

transition-metal elements providing a first-principles explanation of the observed two-phases nanostructure. The calculated solution energies of transition metal elements at various substitution sites in SmCo_5 and $\text{Sm}_2\text{Co}_{17}$ show that Cu goes into 1:5 phase but not into 2:17 phase, in agreement with well-known experimental findings. Titanium and zirconium can go to either phase with Ti(Zr) having a slight preference for the 1:5 (217) phase. Zirconium has a very large negative solution energy which implies that some of it may segregate or go to the phase boundaries. In the 2:17 phase, both Ti and Zr prefer the dumbbell-site substitution.

This research is supported by AFOSR, DOE, NSF MRSEC, and by CMRA.

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