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Theory of Point-Defects, Non-Stoichiometry, and Solute Additions in $SmCo_{5+x}$-Sm_2Co_{17-y} and Related Compounds

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Abstract:

There is considerable interest in the possibility of producing Sm-Co-based nanocomposite magnets by rapid solidification and other far-from-equilibrium processing methods. Thermodynamic and kinetic models are quite valuable in understanding and optimizing such methods. This paper describes a method of estimation, utilizing tight-binding-based bond-order interatomic interaction potentials, of the thermodynamic properties of point defects (such as vacancies, interstitials, antisite defects, and solute additions in the $SmCo_{5+x}$ and Sm_2Co_{17-y} phases and related rare-earth-transition metal compounds. Illustrative calculations for point defects in $SmCo_5$ will be presented. The results suggest a unified model of the thermodynamic properties of the $SmCo_{5+x}$ - Sm_2Co_{17-y} region of the phase diagram, based on the 1-5 structure and the replacement of Sm by interacting dumb-bell interstitials to form the 2-17 structure; the model is similar in nature to theories of the thermodynamics of metal hydrides.

I. Introduction:

There has been much recent interest in the possibility of producing exchange-spring nanocomposites based on rare-earth/transition-metal compounds, including Sm-Co-based systems (e.g., references [1] and [2]). Thermodynamic and kinetic models are often very valuable in understanding and optimizing such methods. Such models must be simple enough to use in complex situations, often precluding the use of first-principles calculations, yet they should contain the essential physics of the problem. Sometimes even very primitive models such as pair-potential-based regular solution models can be of great value [3]. A great improvement over the use of pair-potentials in the realism of the description of metallic bonding in recent years has been achieved by the use of many-atom potentials such as embedded-atom models and bond-order potentials [4]. Cottrell has shown that the use of the latter can be of great value in understanding the systematics of the properties of transition metal carbides [5] and intermetallic compounds [6].

In this paper we will present a bond-order-potential model for rare-earth/transition metal compounds and illustrate its use by calculations of the energetics of point defects and non-stoichiometry in $SmCo_5$. The results suggest s simple regular-solution model for the $SmCo_5$-Sm_2Co_{17} region of the phase diagram of the Sm-Co system.

II. Bond-order-potential model:

We will use the simplest version of many-atom bond-order-potentials [4] as implemented by Cottrell [5,6]. This is essentially a modern and explicit version of Linius Pauling's resonating valence-bond theory of metallic bonding [7]. In this approach the bonding energy U_{bond} of a collection of atoms is described as the sum of bond energies $h(R)$, where R is the bond length. The effectiveness of the bond depends upon its bond order θ, which, in turn, depends upon the competition of nearby bonds for the available valence electrons. In the Pettifor approach this is described by:

$$U_{bond} = \frac{1}{2}\sum_{i}\sum_{\neq j} h(R_{ij})\theta_{ij} \tag{1}$$

where i and j are indices labeling the various atoms in the system. Pettifor's relation for the bond orders is given by

$$\theta_{ij} = 4\chi h(R_{ij})F(\rho_{ij}) \tag{2}$$

where χ is a function describing the filling of the available electron bands and:

$$\rho_{ij} = \frac{1}{2}(\rho_i + \rho_j) \tag{3}$$

$$\rho_i = \sum_{k \neq i} h^2(R_{ik}) \tag{4}$$

$$F(x) = x^{-1/2} \tag{5}$$

In Cottrell's implementation of his scheme, the bond-filling factors 4χ is taken to be constant and set equal to unity; the bond-length dependence of the bond strength h is approximated by:

$$h_{ij}(R_{ij})_e = Be^{-q_{ij}R_{ij}} \tag{6}$$

In addition to bonding terms, as described above, Cottrell includes a interatomic repulsion energy U_{rep} described as a sum of pairwise interactions:

$$U_{rep} = 1/2 \sum_i \sum_{\neq j} A_{ij} e^{-p_{ij}R_{ij}} \tag{7}$$

Further simplifications are achieved by restricting interactions to nearest-neighbor bonds and repulsions and by keeping a constant ratio of the repulsion and bonding exponents p/q, chosen to be four for transition metals (and rare-earths, which we treat here is equivalent in nature to early transition metals).

We have used the Cottrell-Pettifor scheme to fit data [8] for the atomic volume, cohesive energy, and bulk modules of the transition-metal and rare-earth elements to obtain the parameters A, b, and p in Eqs. (6) and (7). Values for several elements of interest are listed in Table 1.

In order to describe the properties of intermetallic compounds, such as $SmCo_5$, it is necessary to describe the strength of bonds (and repulsions) between atoms of different species. For this purpose, we assume a relation, similar to the Wolfsberg-Helmholtz approximation [9] of quantum chemistry, between the bond strengths between unlike atoms, IJ, and those of like atoms of the species involved, IJ and JJ, as:

$$A_{IJ} = 1/2 K_r (A_{II} + A_{JJ}) \tag{8}$$

$$B_{IJ} = 1/2 K_b (B_{II} + B_{JJ}) \tag{9}$$

$$p_{IJ} = 1/2 (p_{II} + p_{JJ}) \tag{10}$$

The unknown constants, K_r and K_b, based on semiempirical quantum-chemical experience [9], are expected to be somewhere between one and two. We find their value by requiring agreement with the experimental heat of formation and volume per atom of the compound of interest. Using the Miedema approximation [10] to estimate the heat of formation and the experimental value of the specific volume [11], we find K_r and K_b to be 1.50 and 1.37, respectively, for $SmCo_5$.

Element	p, nm^{-1}	12A, 10^4 eV	12B, eV
Fe	39.69	7.14	500
Co	41.40	9.20	54.2
Ni	39.60	5.66	482
Ti	31.78	3.57	459
Zr	26.97	2.35	503
Hf	29.35	4.55	602
Pr	21.92	0.737	253
Nd	23.87	1.30	266
Sm	27.83	3.23	244
Dy	27.40	3.15	302

Table 1: Parameters used in Eqs. (6) and (7) for several transition-metal and rare-earth elements. Note: The exponent ratio p/q is assumed to be four for all elements.

III. Estimates of the energetics of point defects and non-stoichiometry in $SmCo_5$:

The bond-order potential model described above can be used quite easily to estimate the energetics of defect formation in $SmCo_5$. Calculations based on a rigid lattice are easily made. While, in such an approximation, atomic relaxation is neglected, the bond-order-potential method automatically includes electronic relaxation, i.e. “back bonding,” by means of the re-computation of the bond orders after the defect is created. This electronic relaxation alone results in good agreement with experimental data for vacancy formation in elemental transition metals. Similar good results were obtained by Cottrell for the energetics of non-stoichiometry by means of the formation of vacancies in transition-metal carbides [5] and for vacancies and antisite defects in intermetallic compounds of the Ni-Al system [6]. Atomic relaxation effects can be easily estimated using methods of continuum [12] or discrete [13] elasticity theory. In the following estimates, atomic relaxation is neglected. The consequences of this are discussed below.

Consider first the formation of point defects in stoichiometric $SmCo_5$. If a Co atom is removed from a site in a plane containing Sm atoms (Co_1 site) in the interior of the crystal and placed in a similar site at a jog on the surface, the computed energy of bond breaking is 4.15 eV; however subsequent back-bonding (i.e., electronic relaxation) reduces the energy by 3.09 eV for a net energy required for Co_1 vacancy formation of 1.06 eV. Likewise the energy for Co_2 and Sm vacancy formation are 1.71 eV and 1.78 eV respectively. In order to form vacancies without changing the composition of the crystal, including the surface, it is required that vacancies be formed in numbers corresponding to the ratio of sites in the crystals ($2Co_1/3Co_2/1Sm$); thus the weighted average energy per vacancy for the required “Schotky sextet” of vacancies is 1.5 eV. The ratio of this to the cohesive energy per atom of $SmCo_5$, 4.38 eV, is 0.34. This is somewhat less than the experimental values [14] for bcc transition metals, such as W and Mo, for which the ratio is about 0.4 - 0.5, and is similar to experimental values [14] for fcc transition and noble metals, such as Pt, Cu, Ag, and Au, for which the ratio is about 0.25 - 0.35. Because of the differences in energy required to remove atoms from the various sites to the surface [1.06 eV (Co_1), 1.71 eV (Co_2), 1.78 eV (Sm)], at high temperatures of processing there will be a tendency for Co to segregate to surfaces, and probably grain boundaries as well, with implications for coercivity if such segregation is retained at lower temperatures.

Next, let us consider the energy required to go off the stoichiometric composition $SmCo_5$ by the addition of Co, i.e. $SmCo_{5+x}$, by means of the creation of point defects. There are three simple possibilities: 1) formation of "constitutional" vacancies on the Sm sites; 2) formation of simple antisite defects on Sm sites, i.e. replacing a Sm atom by a single Co atom; and 3) replacing a Sm atom by a pair of Co atoms in a "dumb-bell" configuration aligned along the c axis. We can very easily use the bond-order potentials to compute the energy required to remove Sm atoms, exchange one type of atom for another, and insert an extra Co atom, if we neglect the relaxation of the atomic coordinates. (Recall that the bond-order-potential method automatically includes electronic relaxation.) The neglect of atomic relaxation will be more serious in the case of dumb-bell interstitials and we will discuss this further below.

In the case of constitutional Sm vacancies, we consider the following process. Start with N unit cells of stoichiometric $SmCo_5$ and remove Nx/5 Sm atoms to form vacancies. Take Nx atoms of metallic Co and vaporize them, then combine them with the removed Sm atoms for Nx/5 unit cells of $SmCo_5$, and add this to the compound with the vacancies. The result is N unit cells of $SmCo_{5+x}$; for each of the Nx Co atoms added the energy cost of this process is:

$$\Delta E_V = \frac{1}{5}\,\Delta E(\text{to remove Sm from Sm site}) + \frac{6}{5}\,U_{SmCo_5} - U_{Co} \tag{11}$$

where *U* is the cohesive energy <u>per atom</u> of the appropriate crystal. The values of the three terms on the rhs are, respectively: 1/5 (7.29), -(6/5) 4.38, and 4.41 eV. The net energy cost is 1.22 eV per added Co atom, by means of the formation of constitutional vacancies.

By use of the same kind of reasoning, the energy cost per added Co atom by means of the formation of simple antisite defects, i.e. single Co atoms on Sm sites, is:

$$\begin{aligned}\Delta E_{AS} = {} & \frac{1}{6}[\Delta E(\text{to remove Sm atom from Sm site}) + \Delta E(\text{place Co atom on a vacant Sm site})] \\ & + U_{SmCo_5} - U_{Co}\end{aligned} \tag{12}$$

The values of the three terms are found to be, respectively, (1/6) 3.40, - 4.38, and 4.41 eV, for a net energy per added Co atom of 0.60 eV.

Likewise the energy required to form an antisite defect consisting of a "dumb-bell" of two Co atoms on a Sm site in an unrelaxed lattice is:

$$\begin{aligned}\Delta E_{DB} = {} & \frac{1}{7}[\Delta E(\text{to remove a Sm atom from a Sm site}) \\ & + \Delta E(\text{to place two Co atoms on a vacant Sm Site})] \\ & + \frac{6}{7}U_{SmCo_5} - U_{Co}\end{aligned} \tag{13}$$

The values of the three terms are found to be, respectively, -(1/7) 1.84, -(6/7) 4.38, and 4.41, for a net energy cost per added Co atom of 0.39 eV. Several comments are in order. In making this calculation it was assumed that the Co-Co separation in the dumb-bell is the same as that in Sm_2Co_{17}.

[15] The fact that the energy to replace a Sm atom by a pair of Co atoms is negative arises from the much larger size of the Sm atom and the larger strength of Co-Co bonds compared to Sm-Co bonds. The energy cost is also lowered because of the strong bond between the pair of Co atoms in the dumb-bell because of the attraction of bonding electrons away from the long bonds to the neighbors to the short bond of the dumb-bell.

The neglect of lattice relaxation is much more serious for the dumb-bell interstitial energy than for the simple antisite defect or the constitutional vacancy. Hence the relative value of the energy cost per added Co atom should be even more favorable for the dumb-bell mechanism than for the simple-antisite-defect and constitutional-vacancy mechanisms than these rigid-lattice estimates (0.39 eV, 0.60, and 1.22 eV, respectively) indicate. This is consistent with the experimental observation that the various crystallographic structures observed for Sm_2Co_{17} [15] can be constructed from the $SmCo_5$ structure by the substitution of Co-Co dumb-bells in appropriate Sm sites. An important consequence of the lattice distortions caused by the dumb-bell interstitials is that the elastic interactions between them can give rise to a phase separation of Sm_2Co_{17} from sufficiently off-stoichiometric compositions of $SmCo_{5+x}$, as is the case in metal-hydrogen systems.

IV. $SmCo_{5+x}$ - Sm_2Co_{17-y} phase separation by means of the elastic interaction between Co-Co dumb-bell interstitials

Because of the lattice distortions resulting from Co-Co dumb-bell interstitials on Sm sites of the $SmCo_5$ lattice these interstitials interact in three ways: 1) a short-range repulsion restricts the total interstitial content; 2) a long-range attractive elastic interaction which promotes phase separation; and 3) angular elastic-dipole interactions which give rise to crystallographic ordering of the dumb-bells. In this sense, this system resembles metal hydrides, for which an extensive theory exists [16]. In this discussion we will focus on the first two types of interactions. For the first type we will simply use a hard-core repulsion which restricts to total dumb-bell interstitial content to 1/3 of number of Sm sites. (This maximum results in stoichiometric $SmCo_{17}$.) For the second type we use the macroscopic, long-range image interaction between elastic dipoles [12,13,16], and we thereby estimate the strength of the interaction from the difference in lattice parameters of $SmCo_5$ and Sm_2Co_{17}.

We approximate the elastic response of the $SmCo_5$ as that of a finite, isotropic elastic continuum. In this approximation, the long-range elastic interaction [12,13,16] gives rise to an interaction energy, per Co site, given by:

$$E_{\text{int}} = -\frac{1}{2}c^2\left(\frac{1}{\Omega}\frac{d\Omega}{dx}\right)^2 B\Omega\left[\frac{(4/3)\mu}{B+(4/3)\mu}\right] \tag{14}$$

where c is the number of Co-Co dumb-bells per Sm site; Ω is the volume per Sm site ; $d\Omega/dx$ is obtained from the difference in specific volume between $SmCo_5$ and Sm_2Co_{17} [15,11], B is the bulk modulus, and μ is an average elastic shear modulus for $SmCo_5$ [17]. This yields an interaction energy of

$$E_{\text{int}} = -{}^1\!/_2\, a_{\text{int}}c^2 \tag{15}$$

where $a_{\text{int}} \cong 0.23$ eV.

An appropriate estimate of the effect of this interaction between Co-Co dumb-bells can be made by analogy to metal-hydride systems. In this case statistical thermodynamic models have been made using long-range elastic image interaction between interstitial hydrogen atoms, together with hard-core interactions at short range, for transition-metal compounds. Tessier et al. [18] have recently analyzed phase separation in FeTi hydrides with such a model; for this system the found a value for a_{int} of about 0.16 eV and used a relationship of Griessen [19] ($T_c = a_{\text{int}}/4$ k) to calculate the maximum temperature of phase separation to be 455 k. Using this result for our value of a_{int}, 0.23 eV yields a maximum temperature of phase separation of 670 K, which is considerably less than the value of 1600 K suggested by a visual estimate from the Sm-Co phase diagram [20]. Clearly, a better estimate of the dumb-bell interstitial interaction energy and/or a more careful examination of the statistical thermodynamics is needed. A brief sketch of the latter is found below.

V. A statistical thermodynamic model for $SmCo_{5+x}$ - Sm_2Co_{17-y}

We will briefly sketch out a statistical thermodynamic model for the free energy G of this system which, for example, could be used to the estimates of the dumb-bell formation energy ΔE_{DB} and interaction energy a_{int} discussed above. We use the hard-core repulsion between dumb-bells to limit the degree to which Sm atoms can be replaced, in accord with the phase diagram, to a value of 1/3. Subject to this restriction we take the distribution of dumb-bells over the available N_s Sm sites to be random. [We have approximated the Sm_2Co_{17-y} phase as being in the disordered Cu_7Tb structure rather than the actual ordered Th_2Zn_{17} structure [15].] With these approximations, the free energy of the system can be obtained by the methods discussed in reference [21], and it is given by:

$$G = 7N_s \Delta E_{DB} c - {}^{1}\!/_{2}\, N_s a_{\text{int}} c^2 - N_s kT[\alpha \ell n\alpha - (\alpha - c)\ell n(\alpha - c) - c\ell nc] \qquad (16)$$

where $\alpha = 1/3$. c is the fraction of the N_s Sm sites occupied by Co-Co dumb-bells. The free energy in Eq. (16) is that of N_o formula units of $SmCo_{5+x}$ relative to that of N_o formula units of $SmCo_5$ plus $N_o x$ units of metallic Co. The fractional concentration c is given by x/(7+x).

While the free energy of the system is derived most simply in the form of Eq. (16), in order to correctly explore the thermodynamics of phase separation it is necessary to write the free energy in terms of the composition c and the total number of atoms N_t rather than the number of Sm sites N_s, since the latter varies as the stoichiometry of $SmCo_{5+x}$ varies with x. The thermodynamics of phase relations are most easily discussed in terms of the free energy per atom as the composition is varied [3]. For our system, $CoSm_{5+x}$ for $0 \le x \le 3.5$, it is easily shown that the relationships among the number of formula units N_o, the total number of atoms N_t, and the number of Sm sites N_s are given by:

$$N_s = N_o\left[1 + \left({}^{x}\!/_{7}\right)\right] = \frac{N_o}{(1-c)} \qquad (17)$$

$$N_t = N_o(6+x) = N_o \frac{(6+c)}{(1-c)} \qquad (18)$$

$$N_s = \frac{N_t(7+x)}{7(6+x)} = \frac{N_t}{(6+c)} \qquad (19)$$

Thus, the required free energy per atom (in terms of the concentration of dumb-bells) is given by:

$$\frac{G}{N_t} = \frac{1}{6+c}\left\{7\Delta E_{DB} c - {}^{1}\!/_{2}\, a_{\text{int}} c^2 + kT[c\ell nc + (\alpha - c)\ell n(\alpha - c) - \alpha \ell n\alpha]\right\} \qquad (20)$$

An analysis of the experimental phase diagram in the $SmCo_{5+x}$ - Sm_2Co_{17-y} region. using Eq. (20), should provide a means of testing and improving our estimates of ΔE_{DB} and a_{int}, which can then be used, for example, to calculate spinodal lines, thermodynamic factors for interdiffusion kinetics, and similar quantities for use in understanding processing and the evolution of microstructures in this system.

VI. Conclusions

The elementary estimates of defect energetics and free energies discussed above show how bond-order potentials and elasticity theory (either continuum [12] or descrete-lattice [13] versions), together with empirical corrections from the phase diagram and measured lattice parameter variations, can be used to generate thermodynamic (including metastability) and kinetic models for the Sm-Co system and related materials. Such models should be of help in understanding and optimizing processing methods for rare-earth/transition-metal compounds for magnetic applications.

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