# "Leapfrog Thermodynamics" among Binary Magnetic Phases Competing for Stability

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Relative to $Sm_2Co_7$ plus $Sm_2Co_{17}$, $SmCo_5$ is stable below 700 K and above 1000 K. Contrary to previous thinking, this is thermodynamically consistent. The free energies of formation of these phases seem to be marginal when estimated from data reported for the analogous compounds of other lanthanons. Above its Curie point at 713 K, $Sm_2Co_7$ is stabilized by its gain in entropy from magnetic disordering, so that $SmCo_5$ loses the competition for stability. The Curie point of $SmCo_5$ is 1020 K, above which $SmCo_5$ experiences a similar gain in entropy, stabilizing it relative to $Sm_2Co_7$ plus $Sm_2Co_{17}$. Such "leapfrog thermodynamics" are especially evident in binary systems like Sm–Co, in which each discrete compound is subject to an order–disorder transition, for which the critical temperatures follow a monotonic trend across the phase diagram. © 1995 Academic Press, Inc.

## INTRODUCTION

There is strong evidence that $SmCo_5$ is unstable below ~1000 K, in a eutectoid between $Sm_2Co_7$ and $Sm_2Co_{17}$ (1). However, the synthesis of $SmCo_5$ in room-temperature ball-milling experiments has been reported (2, 3). Other evidence for the stability of $SmCo_5$ at low temperatures, such as its crystallization from amorphous films when annealed at 773 K, has been reviewed by Kumar (1), who saw it as inconsistent with the eutectoid near 1000 K. This paper shows that there is no inconsistency; indeed, stability over dual ranges of temperature is to be expected when magnetic intermetallic compounds compete for stability in systems such as Sm–Co.

## DISCUSSION

The enthalpy of formation for $SmCo_5$ at 298 K is only −6.8 kJ/mole, i.e., −1.13 kJ/g·atom (4). Values for $Sm_2Co_7$ are not listed in the same compilation, but the value for $LaCo_5$ at 1150 K is only −3.9 kJ/mole, while for $La_2Co_7$ at 1050 K it is −5.2 kJ/mole, a difference of 0.07 kJ/g·atom.

Contributions to entropy, due to magnetic disordering above the transition temperature, are on the order of 20

J/mole/° for lanthanons (5), and 10 J/mole/° for transition metals (6) and their compounds (7). Consequently, the marginal differences in enthalpies of formation of the Sm–Co intermetallics may be outweighed by the magnetic entropy–temperature product in the expression for free energy

$$G = H - TS,$$

where $G$, $H$, $T$, and $S$ are free energy, enthalpy, absolute temperature, and entropy, respectively.

The magnetic contributions to both entropy and enthalpy are related to the specific heat anomaly (the lambda cusp in the plot of specific heat against temperature) which results from the energy absorbed by magnetic disordering. The magnetic entropy depends mainly on the effective magnetic moment of the metal atoms, while the transition temperature (Curie or Néel) is also affected by the coordination number of each magnetic atom by other magnetic atoms (8). The influence of these factors for Fe, Co, and Ni can be gauged from a common plot of their specific heats versus temperature (6).

In the Sm–Co system, the Co-rich compounds possess the same structural features, including regions of close-packed Co atoms which determine the magnetic properties (9). Consequently, the Curie temperatures and the size of the specific heat anomaly increase regularly with increasing Co content, as follows (10):

| $Sm_2Co_7$ | $SmCo_5$ | $Sm_2Co_{17}$ |
|---|---|---|
| 713 K | 1020 K | 1200 K |

Correspondingly, the increase in enthalpy, due to magnetic disordering, is less for the lower Curie points. However, the contributions to entropy are comparable because entropy is calculated from the heat absorbed, divided by the absolute temperature.

Near the Curie point, the effect on free energy is slight, because the increase in the enthalpy and entropy–temperature terms is approximately balanced. The exact effect
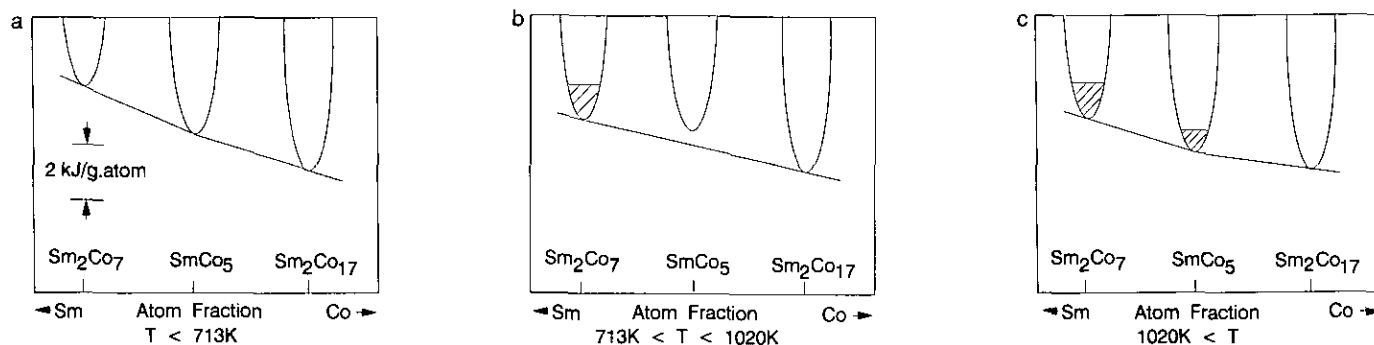
FIG. 1. Diagrammatic plots of molar free energies (per atom) of the three Co-rich intermetallic compounds: (a) Below the Curie temperatures of all three phases. At its lowest point, the curve for $SmCo_5$ lies just below the tangent (not shown) that is common to the curves for $Sm_2Co_7$ and $Sm_2Co_{17}$. $SmCo_5$ is therefore stable, relative to a mixture of these two phases. (b) Between the Curie temperatures of $Sm_2Co_7$ and $SmCo_5$, $Sm_2Co_7$ has its entropy increased by magnetic disorder, and its free energy is diminished by the magnetic contribution (shown hatched), so that $SmCo_5$ is unstable relative to a mixture of the other two phases. (c) Above its own Curie temperature, $SmCo_5$ gains a similar increase in entropy and "leapfrogs" past $Sm_2Co_7$, so that it is again stable, relative to a mixture of the other two phases.

depends on the shape of the specific heat anomaly, as illustrated by plots of the magnetic contributions to enthalpy, free energy, and specific heat for $\alpha$Fe (11). At all higher temperatures, the free energy is progressively more favorable because of the greater entropy–temperature product.

Figure 1 illustrates diagrammatically how the three Sm–Co compounds compete for stability. Below 713 K, $SmCo_5$ is stable between its neighboring intermetallics, as shown in a plot of molar free energy against atom fraction of Co, Fig. 1a. Between 713 and 1020 K, $Sm_2Co_7$ is more stable because of its entropy of magnetic disorder. The free energy curve for $SmCo_5$ then lies above the tangent between the curves for $Sm_2Co_7$ and $Sm_2Co_{17}$, as in Fig. 1b. Hence, in this temperature interval, $SmCo_5$ is unstable relative to a mixture of $Sm_2Co_7$ and $Sm_2Co_{17}$. Above 1020 K $SmCo_5$ gains its own magnetic entropy, as shown in Fig. 1c, and becomes stable above its eutectoid near this Curie temperature. Above its Curie point at 1200 K, $Sm_2Co_{17}$ is similarly stabilized, weakening the relative stability of $SmCo_5$, but apparently not enough to destroy it; this happens at 1593 K (1), at which temperature the molten alloy has replaced $Sm_2Co_7$ as the stable phase on the Co-poor side of $SmCo_5$. The superior entropy of the melt allows it to replace even $Sm_2Co_{17}$ above 1608 K. The $T$–$X$ phase diagram is shown in Fig. 2, with the addition of the second, low-temperature stability field for $SmCo_5$.

In other words, there is a "leapfrog effect" of magnetic entropy on the stabilities of individual phases in a set of competing magnetic phases. This is an important point, which may have application to other magnet preparative methods.

For example, when ball-milled at 298 K (just below its Curie temperature of ~400 K (10)), $Sm_2Fe_{17}$ is unstable

with respect to $\alpha$-iron and a Sm–Fe alloy which is amorphous to X-rays (12); a similar fate befalls the related boride, $Nd_2Fe_{14}B$, although both intermetallics are reformed when annealed at 973 K. An additional factor (13), which detracts from the stability of Fe-based intermetallics, is the anomalously low internal energy of body-centered-cubic (bcc) $\alpha$Fe, relative to the close-packed forms of Fe to which the intermetallics are more closely related.

Nevertheless, these intermetallics might enter a second, low-temperature region of stability if chilled by liquid nitrogen, toward a temperature that would favor magnetic ordering within the amorphous Nd–Fe phase in the ball-milled product (13).

Chemical ordering may need to be considered in the same way; e.g., in the magnet systems Fe–Co–$Ln$ ($Ln$ = a lanthanon), the energy of CsCl-type ordering in a com-
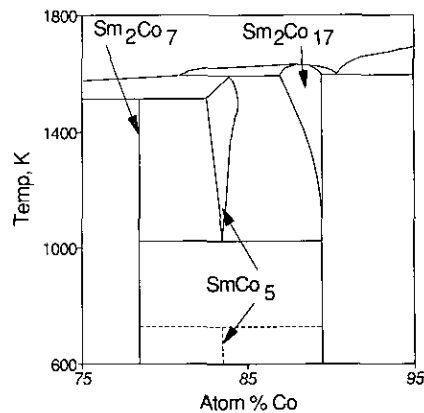


FIG. 2. The phase diagram for the Co-rich part of Sm–Co, after Kumar (1), with the addition of a low-temperature stability field and peritectoid for $SmCo_5$, shown dashed.

peting FeCo alloy (14) is comparable to the magnetic ordering in the $Sm_2(Fe,Co)_{17}$ phase. In iron and its ruthenium alloys, the existence of a body-centered-cubic (bcc) form between high- and low-temperature fcc forms is a more general case of leapfrog thermodynamics (15). The entropy of Fe in the fcc form is boosted from low temperatures by the thermal excitation of some Fe atoms to a high spin state (16), while bcc $\alpha$Fe gains magnetic entropy above its Curie temperature of 1038 K. The return of the fcc form at the highest temperatures is due to subtle differences in the temperature dependence of vibrational and electronic contributions to specific heat and entropy (15, 16).

## CONCLUSION

Stability over more than one range of temperatures is to be expected in binary systems, among competing compounds that are all subject to order–disorder transitions at different temperatures.

## ACKNOWLEDGMENTS

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