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A comparison of surface segregation for two semi-Heusler alloys: TiCoSb and NiMnSb

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Abstract

Very different types of surface segregation are found for very similar Heusler alloy materials. We observed significant manganese and antimony segregation to the surfaces and near surface regions of the semi-Heusler alloys NiMnSb and TiCoSb respectively. The Mn and Sb surface enrichment was characterized by angle resolved core level photoemission. Indications of surface disorder from low energy electron diffraction provide complimentary evidence of segregation. © 2002 Elsevier Science B.V. All rights reserved.

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For most alloys, even alloys containing elements with magnetic moments, the common mechanisms of lowering the difference in free energy (between the surface and the bulk) include segregation, surface reconstructions and anomalous surface magnetic ordering (including spin reorientation). A number of competing effects play a role in determining the type and extent of segregation, including bond strengths and strain.

In a class of materials covering such a diverse range of constituents and electronic properties, such as the half-Heusler alloys, is the surface segregation similar? The NiMnSb and TiCoSb semi-

Heusler alloys are remarkably similar in structure with similar lattice constants. Like the other half-Heusler alloys, NiMnSb and TiCoSb have the form ABC (where A, B are transition metals and C a group IV element). Nonetheless, some half-Heusler alloys are predicted to be half metallic systems [1–8] while others are semiconductors/insulators [9,10]. Both NiMnSb and TiCoSb containing 3d transition metals, notably manganese and cobalt respectively, with large moments. Yet these two Heusler alloys differ in that NiMnSb orders ferromagnetically while TiCoSb is inherently a dielectric.

If magnetic ordering plays a role in driving segregation (or contributing to the energy differences that lead to segregation) then very similar Heusler alloys, or indeed very similar alloys of any sort that contain elements with large magnetic

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moments, can exhibit very different types of segregation behavior. This is because different types of magnetic ordering at the surface are possible as indicated in Fig. 1. Large moment elements will lower the difference in free energy through solvation in the bulk of a ferromagnet, while anti-ferromagnetic ordering at the surface can be advantageous thermodynamically due to the pairing of electron spins and opening of an anti-ferromagnetic band-gap at $E_F$ [11]. The possibility that magnetic moments and magnetic ordering can affect segregation has been already discussed [12].

Segregation will have a profound influence on potential applications of these materials. In principle, the high spin polarization semi-Heusler alloys (like NiMnSb) provide excellent material properties for tunnel junctions and spin-electronics in general [13–15], and in addition, provides an excellent lattice match with their dielectric/semiconductor cousin TiCoSb [12]. However, both interface states [16,17] and segregation [18,19], leading to a change in the stoichiometric structure, will impact polarization and spin injection properties [18,20,21]. When there is extensive Mn segregation, as in the case of NiMnSb [19] (although Sb segregation has also been suggested to occur for NiMnSb [22]), then there is a suppression of the polarization [18]. This will diminish the functionality of NiMnSb as a spin-injection material in a spin-electronic device. The dielectric/semiconducting properties of TiCoSb could be diminished by Sb phase separation, as a result, the semi-metallic band structure would complicate spin injection immensely [16,22–24].

One approach to addressing these significant problems, caused by segregation, is to fabricate a non-ideal bulk material so that the correct desired material is formed—and is stable—at the interface, but such interface “design” requires a rigorous understanding of segregation. Thus, determining the fundamental basis of segregation is of utmost importance to spin-electronics because it will greatly influence the choices of future materials for and the architecture of devices premised on electric, magnetic, and other bulk band related properties. We present data from TiCoSb and NiMnSb to illustrate some of these complexities.

Each sample was prepared by magnetron sputtering to form single crystals. Both alloys (1000 Å thick) were grown on Mo(1 0 0) seed layer (200 Å) grown on a chemically cleaned MgO(1 0 0) substrate, which were then deposited with a 1000 Å Sb capping layer to prevent oxidation of the stoichiometric semi-Heusler surface. The two semi-Heusler alloys shown in Fig. 2 have $C_{2V}$ symmetry (point group notation) and C1b structure (four interdigitated fcc lattices). Bulk order was verified, ex situ, by X-ray diffraction and the bulk lattice constant of 5.9 Å confirmed, while surface order was established by low energy electron diffraction (LEED) as represented in Fig. 2a and b. Using angle resolved X-ray photoemission spectroscopy (ARXPS), with Mg K$_\alpha$ soft X-rays (1253.6 eV), the core levels of each constituent element—of the respective alloy—were obtained for emission angles from 0° through 60°. Prior to taking core level data, each sample surface was cleaned by successive Ar$^+$ sputtering and annealed by resistive heating. The surfaces phases studied for each sample represent a progression from the as-deposited state (with Sb capping layer) to clean (capping layer removed) to, eventually, a surface...
with extensive segregation with half-Heusler structure (stoichiometry) destroyed in the surface and near surface regions. After each annealing treatment, each sample was cooled slowly, and allowed to reach room temperature before surface characterization spectra were taken.

Angle resolved spectra provide intensity (counts) as a function of binding energy for differing electron detector emission angles. For each alloy, shown in Fig. 3, there exists evidence of changes in surface composition with continued annealing, even after the Sb capping layer was removed. On the basis of the effective probing depth (mean free path normal to the surface) of the photoelectrons decreasing as emission angle increases, we were able to exploit the XPS intensity ratios, normalized by cross-section and analyzer transmission function, to make some quantitative analysis of which constituents were segregating [25]. Normalized intensity ratios constructed from angle resolved XPS intensities integrated over selected elemental core level peaks are shown in Fig. 4. Reproducible results were obtained from multiple samples of each Heusler alloy.

Fig. 2. (a) Crystal structure of the semi-Heusler alloys TiCoSb and NiMnSb, with lattice constant 5.9 Å. The structure is four interpenetrating fcc lattices corresponding to the C1b structure (C1V symmetry). (b) LEED pictures of TiCoSb with antimony capping layer removed and following antimony segregation. (c) LEED pictures of NiMnSb with antimony capping layer removed but without manganese segregation (for comparison). The electron beam energy was ≈30 eV in both images.
The normalized intensity ratios were plotted as a function of emission angle for each constituent. The data used to construct these plots is determined by the intensity ratios of the Ni 2p$_{3/2}$, Mn 2p$_{3/2}$, and Sb 3d$_{5/2}$ core levels of NiMnSb and the Ti 2p$_{3/2}$, Co 2p$_{3/2}$, and Sb 3d$_{5/2}$ core levels of TiCoSb. Each experimental ratio was normalized using

$$ R(\theta) = \left[ \frac{I_A(\theta)/\sigma_A}{I_B(\theta)/\sigma_B} \right] \left[ \frac{E_{\text{kin}}^p(A) - C}{E_{\text{kin}}^p(B) - C} \right] $$

where $\theta$ is the emission angle, $\sigma_A$, $\sigma_B$ are the cross-sections and the $E_{\text{kin}}^p(A) - C$ ($p = 1/2$ and $C = 0$) terms correct for the transmission function of the electron analyzer at the kinetic energy of core level $A$. The photoionization cross-sections were taken from Scofield [26], and interpolated as $\sigma_{\text{Ti}} = 5.22$, $\sigma_{\text{Co}} = 12.62$, $\sigma_{\text{Sb}} = 11.13$, $\sigma_{\text{Ni}} = 13.92$, $\sigma_{\text{Mn}} = 8.99$.

From these emission angle dependent ARXPS intensities, some elemental core level intensities are disproportionally large when compared to the stoichiometric composition of the alloy. A distinctive enrichment of the surface of NiMnSb with Mn and TiCoSb with Sb is clearly evident from both the high ratios and positive concavities (increasing slope) as emission angle increases with respect to the normalized intensity ratios. In the case of TiCoSb, it is obvious that the ratios of Sb/Ti and Sb/Co are quite large, even after annealing to temperatures well above the temperatures (900 K) necessary to remove the Sb capping layer from the other Heusler alloy surface (400–450°C). This indicates that Sb dominates the surface region (segregation of Sb is extensive), with the bulk acting as an Sb reservoir, after a treatment that should lead to removal of the capping layer [18]. While the intensity ratio is indicative of extensive Sb segregation (Fig. 4d and f) the greater emission angles exhibit a drop in Sb/Co and Sb/Ti intensity ratios but with a relative similar amount of Co to Ti. This suggests that while Sb segregation is extensive, at the topmost surface layer, there exists some titanium and cobalt in the near surface region. With continued annealing, Sb dominates the surface region even more extensively, with some cobalt in the surface region, and Co segregation, relative to titanium, is distinctly possible.
In the NiMnSb situation, once the Sb capping layer is removed, a surface of near stoichiometric composition can be formed [18,19]. A stoichiometric surface is defined as alternating layers of Ni-vacancy with Sb–Mn for NiMnSb and Ti-vacancy with Sb–Co layers for the TiCoSb alloy (as indicated in Fig. 2), though this surface is known to terminate in Mn–Sb [18,19]. With continued annealing treatments, one finds the Mn/Ni and Mn/Sb ratios are increasingly larger. This implies, crudely, that Mn dominates the surface but the Ni/Sb ratio remains nearly one-to-one (Fig. 4).

In addition, the surface order tends toward greater disorder as segregated atoms destroyed the semi-Heusler epitaxy as evidenced by LEED analysis (Fig. 2). One should note that as the segregation became more prevalent, the diffraction beams became increasingly diffuse, although the overall cubic structure remained. A diffuse electron diffraction beam indicates only the presence of atomic disorder in the surface layers, since it is not possible to distinguish between different atomic species in a LEED pattern. It is possible that the surface disorder, seen in LEED, to be thermally induced while cleaning the samples and not caused by segregation.

To explicitly calculate a model XPS intensity ratio fit, the equation

\[
R(\theta) = \frac{\sum_{j=0}^{\infty} f_j(A) e^{-|\theta_j|/|\theta_0 cos(\theta)|}}{\sum_{j=0}^{\infty} f_j(B) e^{-|\theta_j|/|\theta_0 cos(\theta)|}}
\]
was used [19,25], where \( \lambda_{A,B} \) is the effective mean free path, as adapted from the calculated mean free paths of Penn [27], (namely \( \lambda_{Ti} = 13.6 \) Å for 2p\(_{3/2} \), \( \lambda_{Co} = 7.3 \) Å for 2p\(_{3/2} \), \( \lambda_{Sb} = 10.8 \) Å for 3d\(_{3/2} \), \( \lambda_{Ni} = 7.0 \) Å for 2p\(_{3/2} \), \( \lambda_{Mn} = 9.35 \) Å for 2p\(_{3/2} \)). The \( f_j(A) \) and \( f_j(B) \) are the fraction of material found in the \( j \)th layer, implying \( f_j(A) = 0.5 \) for Mn in a Mn–Sb layer. The distance between layers is given by \( d \approx 1.5 \) Å, and \( \theta \) as the electron emission angle.

The experimental normalized intensity ratios were compared with a number of surface region compositional models, with various types of surface segregation or enrichment of the topmost layers by a given constituent(s).

The application and intricacies of the models applied to the composition of NiMnSb surface region can be found in Ristoiu et al. [19]. All models fitted to the XPS data for NiMnSb have extensive Mn surface enrichment occurring with annealing. Yet, as we have noted [18,19], following the removal of the Sb capping layer but prior to any subsequent annealing, the stoichiometric surface fits the data best using a model which has a terminal MnSb surface layer, as shown by the solid black line in Fig. 4a–c.

The fits for a stoichiometric surface for TiCoSb are also shown in Fig. 4 (the black solid lines in Fig. 4d–f). Other models explored have not been plotted because of the absence of a unique model, with a demonstrably better agreement with the data, for the experimental Sb segregation to the surface of TiCoSb. One model that agrees with the data obtained following very extensive annealing of TiCoSb, is based on the conjecture that a surfactant layer of CoSb\(_3\), [28,29] is a probable surface termination with Sb dominating the subsurface layers in the near surface region. CoSb\(_3\) belongs to the skutterdite family forming a cubic structure, and is consistent with the stable but diffuse LEED pattern exhibited with increasing Sb segregation. The skutterdites are semiconducting [28], minimizing the changes to the apparent electronic properties of TiCoSb.

The fundamental question arises: why is segregation in NiMnSb and TiCoSb so different? A single driving force for segregation cannot be applied equally to explain the segregation behavior in both alloys. The most obvious origin for segregation is that size-induced stress distorts the lattice, causing strain, which is then alleviated by sending the misfit solute atoms to the surface [25]. This origin for segregation favors Sb segregation in the case of NiMnSb and TiCoSb (or any similar Heusler alloy, including NiMnSb) as Sb \( \approx 1.45 \) Å possesses the largest atomic radius with respect to the other constituents Ni \( \approx 1.35 \) Å, Mn \( \approx 1.40 \) Å, Ti \( \approx 1.40 \) Å, Co \( \approx 1.35 \) Å, as taken from Slater [30]. The thermodynamic parameters, such as those that lead to predictions of segregation based on the type of melting curve for each alloy [31], could favor segregation of Sb that includes a surfactant, such as the proposed CoSb\(_3\). For the NiMnSb, neither argument for Mn segregation appears to be wholly appropriate.

Based on Moran Lopez [12,32], magnetic (spin–spin) alignment possibly plays a subtler and less intuitive role in causing a lowering of the difference in free energy and in determining the dominant constituent for surface segregation. It is possible that Mn segregation reduces the difference in free energy between the surface and bulk by ordering anti-ferromagnetically at the surface. Although it is possible for Co or Ni to order ferromagnetically, solvation of the moments in the bulk is far more likely to lead to a reduction in the difference in free energy for these latter transition metals. It may be that there are some surface preparation conditions for NiMnSb where segregation is dominated by Sb enrichment at the surface [22], suggesting that the competing factors that lead to Mn segregation are close in energy to those that favor Sb segregation. In any case, it very clear that the segregation behavior is, in fact, very different for the two nominally similar Heusler alloys prepared under similar conditions.

The results presented here indicate that Mn segregates to the surface of the NiMnSb alloy, while Sb segregates to the surface of TiCoSb. Indications of surface disorder from low energy diffraction provide complimentary evidence of segregation. Sb segregation may be induced in TiCoSb by stress/strain, and Mn segregation in NiMnSb could be induced by ferromagnetic interactions between spins. Segregation will significantly affect polarization [18,33] and other electronic properties, so surface/interface segregation of the types, observed
for the half-Heusler alloys, will have substantial implications for spin-electronics devices made from these materials.

**Note added in proof**

Similar to the formation of a Co–Sb compound formed at the surface of TiCoSb noted here, a species with the approximate stoichiometry of FeAs was recently found at the interface between iron and InAs. This interface species was found to be a ferromagnetic compound.


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**References**