Structure of the Clean Gd5Ge4(010) Surface

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Abstract.

We have characterized the (010) surface of Gd5Ge4 using scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy. Data from different samples have the following features in common: (1) Surface composition equals bulk composition to within 5 atomic %, both after ion etching and after annealing at temperatures of 400 K to 1200 K; and (2) The surface exhibits two types of terraces. Step heights between similar terraces correspond well to the separation between equivalent layers along the <010> direction in the bulk structure. Density functional theory (DFT) shows that the surface energy of the (0001) plane of hcp Gd is lower than that of the (111) plane of diamond-type Ge, suggesting that surfaces of Gd5Ge4 (for comparable density) should be Gd-rich. Indeed, among the bulk terminations of Gd5Ge4, DFT shows that a pure Ge termination is not favored. The three remaining terminations (two pure Gd and one mixed
Gd-Ge) each have minimum surface energy in a different range of possible Gd chemical potential, indicating that different terminations may be stable under different conditions. DFT shows that step heights between dissimilar terraces, measured in STM, are consistent with the two pure Gd terminations.

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1. Introduction.

Magnetic refrigeration is an emerging, environmentally-friendly technology based upon materials that exhibit a magnetocaloric effect [1-4]. The class of materials consisting of the rare earth metal Gd, and its alloys or compounds with the post-transition elements Si and Ge, is particularly promising because some of its members exhibit a giant magnetocaloric transition near room temperature [5]. Gd$_5$Ge$_4$ is considered one important prototype of this group, and is the object of the present study [6, 7].

Surfaces can be important in magnetic refrigeration, because heat transfer can be limited by the characteristics of the surface. For instance, surface oxidation during exposure to heat transfer fluids can lower the thermal conductivity of Gd-containing materials and hence change the refrigeration efficiency [8]. Previously, we have investigated the effect of oxygen on the clean Gd$_5$Ge$_4$(010) surface, in ultrahigh vacuum at 300 K to 600 K. We found that Gd oxidizes preferentially and that its oxide effectively masks the Ge [9]. Both of these responses are similar to those of another rare earth alloy, LaNi$_5$ [10]. However, the nature of the clean surface was not known. The primary goal of the present work is to study the structure and composition of the clean Gd$_5$Ge$_4$(010) surface, and to compare these features with known bulk characteristics. The (010) surface is chosen because the (010) planes have the highest atomic density in the bulk.

Gd$_5$Ge$_4$ is a line compound with 55 at. % Gd and 45 at. % Ge. Peritectic decomposition to Gd$_5$Ge$_3$ occurs at ~1970 K, with a liquidus at 2073 K [11]. The crystal symmetry of Gd$_5$Ge$_4$ is orthorhombic with 36 atoms per unit cell [11-13]. Lattice parameters are $a = 0.770$ nm, $b = 1.483$ nm, and $c = 0.779$ nm [11]. The crystal structure
is shown in Fig. 1(A). It is often described as two \([\text{Gd}_{10}\text{Ge}_8]\) slabs stacked along <010> (along the \(b\) axis), and staggered slightly along the <100> direction (the \(a\) axis). The slabs repeat at separations of \(b/2 = 0.741\) nm along the <010> direction. They are loosely-coupled, which is key to the structural and magnetic phase transitions in this type of material [6, 7, 14, 15]. Two (010) planes of atoms are depicted in Fig. 1(B). The face of the bulk unit cell, shown by the rectangle, is nearly square. A small amount of a secondary phase is always observed in single crystal samples of \(\text{Gd}_5\text{Ge}_4\) and closely related compounds [16-23]. This secondary phase is \(\text{Gd}_5\text{Ge}_3\), or its analog in the related compounds. It takes the form of narrow, elongated plates that cover 1-6\% of the (010) surface area, based on optical microscopy and scanning Auger electron microscopy [21].

A basic question is whether the bulk structure remains intact at the \(\text{Gd}_5\text{Ge}_4\) (010) surface. We will compare some of our results with those from complex metallic alloys. The alloys that have been studied most thoroughly are Al-rich and hence they are quite different, chemically, from \(\text{Gd}_5\text{Ge}_4\). Nonetheless, they exhibit certain common features and comparisons are enlightening.

2. Experimental Details.

Single crystal ingots of \(\text{Gd}_5\text{Ge}_4\) were synthesized at the Materials Preparation Center (MPC) of the Ames Laboratory [24] via tri-arc crystal pulling [25]. Thermal analysis results were consistent with the published phase diagram [11]. Two separate samples, cut from the same ingot, were used for the STM studies reported here. These will be referred to as #1 and #2. Both of these samples, plus a third cut from a different ingot, were used also for X-ray photoelectron spectroscopy (XPS) analyses.
Surface studies were carried out in an Omicron ultrahigh vacuum (UHV) chamber with base pressure $\leq 1.0 \times 10^{-10}$ mbar. The chamber was equipped with an ion sputter gun, mass spectrometer, X-ray source (Al Kα), Omicron EA 125 hemispherical electron energy analyzer, and a Variable Temperature Scanning Tunneling Microscope (VT-STM).

The sample surfaces were cleaned in UHV with cycles of Ar$^+$ ion etching (1.5 kV, 300 K, incident angle 45°) and annealing for 30 to 60 minutes. There was no noticeable difference in surface structure within this range of annealing time. Cooling from each annealing temperature was controlled. The average cooling rate, starting from 900 K, was 0.25 K/s. In STM, a tungsten tip was used. Tip bias ($V_{\text{tip}}$) ranged from $-1$ V to $+1$ V, with tunneling current (I) constant at 0.5 nA. All STM was carried out with the sample at room temperature. Data were processed using WSxM scanning probe microscopy software [26]. The z-piezo calibration was checked against step heights on Si(111), where the measurement agreed with the literature value to within 3%.

In XPS, the take-off angle (the angle between the entrance axis of the analyzer and the sample surface plane) was 45°. The most intense photoelectron peaks of Gd and Ge were used for analysis: the Gd $3d_{5/2}$ peak at a binding energy of 1186 eV, and the Ge $2p_{1/2}$ peak at 1248 eV [27]. XP spectra were analyzed with CasaXPS software [28].

We determined the $<100>$ and $<001>$ orientations in the surface plane, in two ways. On the (010) surface, the plates of the Gd$_5$Ge$_3$ secondary phase lie in two non-orthogonal directions [29]. The $<100>$ and $<001>$ bisect the acute and obtuse angles of intersection, respectively [29]. We identified the orientation of the plates using optical microscopy, and assigned $<100>$ and $<001>$ in our sample accordingly. The second
approach was to use X-ray diffraction. (A small portion was cut from one of the samples for this purpose.) These approaches gave consistent results. The accuracy of the orientation was about ±5°.

3. Experimental Results and Discussion.

3.1 XPS Data.

**XPS: Surface Composition.** XPS provides a depth-weighted average over the surface and near-surface regions. Preferential ion etching or surface segregation can reveal themselves in variations of measured composition as a function of annealing temperature or ion etching time (i.e. depth profiles) [30, 31].

We first determine the variation in surface composition after the sample is ion etched at room temperature, to generate a common starting point, and then annealed to temperatures in the range 400 K to 1200 K. Surface compositions immediately after annealing are shown in Fig. 2A. (The data at 300 K were taken after etching, without annealing.) In Fig. 2A, different symbols represent data from the 3 different samples. Symbols that are filled differently (e.g. light vs. dark triangles) represent different sets of experiments on the same sample. Only Gd concentration is shown, since the compound is binary and Ge concentration is thus complementary. There is no systematic or reproducible variation of surface composition with temperature, up to 1200 K.

We also measured depth profiles of annealed surfaces. Fig. 2(B) shows representative depth profile data from the two samples, after they were argon-ion etched and annealed at various temperatures as indicated. There is no evidence for a systematic
difference between the composition at/near the surface, and the composition deeper in the bulk.

In both types of experiments (Fig. 2A and Fig. 2B), measured surface compositions of Gd are within 5 at% of the bulk composition. In XPS, a relative accuracy of 10% is often quoted based on Seah’s analysis [32], which in this case would translate into about 5 at%. We therefore conclude that the measured compositions are the same as the bulk composition, to within the accuracy expected for this technique.

3.2. STM Data.

STM: Terrace Types and Step Heights. STM was used to characterize the surfaces of samples #1 and #2. The data sets show both differences and common features. Our presentation is facilitated by first identifying the commonalities. Over most of the temperature range from 900 to 1200 K, a terrace-step structure is observed in which there are two types of terraces, A and B. These are illustrated in Fig. 3. The B-terraces are rough, exhibiting bumps that are 0.3-0.4 nm tall and cover 10–20% of the area of the terrace [Fig. 3(B, C)]. On the B-terraces, there is no resolvable fine structure either atop or between bumps. The A-terraces are relatively smooth, and show a fine structure of parallel stripes that are about 0.04 ± 0.01 nm high, 1.04 ± 0.03 nm apart, and make an angle of 28° ± 4° with the <001> direction [Fig. 3(D, E)]. These stripes are interrupted by many small vacancies and protrusions.

Fig. 3(A) shows that the A- and B-terraces alternate in sequence. While they have comparable areas in Fig. 3, it is more common that one type predominates. For instance, in Fig. 4(A), the B-terraces are larger than the A-terraces. In Fig. 4(B) the trend is the
same, but the A-terraces—indicated by arrows—are even smaller, appearing as thin protrusions at the step edges. In effect, pairs of A- and B-steps are bunched. Conversely, in Fig. 4(C-D), the A-terraces predominate but small regions of B-terrace protrude from the step edges. Examples are circled.

The step heights are measured from line profiles, in which care is taken to avoid irregular features, especially bumps on B-terraces. The step height measured between similar terraces, i.e. A-A or B-B separations, is $0.75 \pm 0.01$ nm. The value of 0.75 nm is half of the bulk unit cell parameter $b = 1.48$ nm. This is reasonable, since the bulk unit cell contains mirror planes perpendicular to the $b$-axis and separated by half the $b$-axis length. These mirror planes correspond to the solid horizontal lines superposed on the atomic structure in Fig. 1(A).

Step heights between dissimilar terraces are $0.35 \pm 0.01$ nm, with the full range of averages over individual experiments being 0.31 to 0.39 nm. There is no systematic difference between A-to-B and B-to-A steps. These values are derived from experiments with different samples and after treatment at different temperatures. Measured step heights do not vary significantly with preparation conditions or sample. Measured step heights do not vary within the stated uncertainties as a function of bias voltage, over the range $-1.0$ to $+1.0$ V. The values of the A-B and B-A step heights will be interpreted in Section 4 and 5.

**STM: Evolution of terrace structure with temperature.** The two samples differ in the evolution of surface structure as a function of annealing temperature. Sample #1 progresses from a rough surface without terraces at 900 K, then displays mainly B-terraces at 1050-1150 K, and finally shows a mixture of A- and B-terraces at 1200 K.
Sample #2 progresses from regions dominated by A-terraces plus regions of mixed A- and B-terraces at 900 K, to mainly B-terraces at higher temperature. We emphasize that A and B terraces appear under most conditions on both samples. The difference lies in which type of terrace, A or B, predominates as a function of temperature. A possible reason for the different progressions lies in the treatment history. Sample #1 was subjected to more ion-etch-anneal cycles, and was heated to higher temperature (1200 K), before STM experiments commenced.

**STM: Thin plates.** We searched for evidence of thin plates of Gd₅Ge₃ on both samples. At very low magnification, STM showed a few linear features of the width expected for a thin plate (of order 1 µm), but these could also have been polishing scratches. Other evidence of the Gd₅Ge₃ phase could not be identified. It may be that the plates were missed because they cover such a small fraction of the surface area—1 to 6% is expected from the literature [21]. We used optical microscopy to examine a sample cut from the same boule as those used in our surface studies, and found that the thin plates covered $2.3 \pm 0.2\%$ of its total surface area. It is known that optical microscopy produces an over-estimate of plate area [21], so 2.3% is an upper bound.

### 4. Theoretical Approach and Results.

In order to test which bulk layers are viable terminations, we use first principles density functional theory (DFT) to calculate energetic parameters that reflect the surface stabilities of elemental Gd, elemental Ge, and different terminations of Gd₅Ge₄. Calculations for pure Gd and pure Ge surfaces provide useful information, but also serve
as a benchmark and launching point for analyzing the Gd₅Ge₄ surface. In all cases, the surface energies are calculated with the Vienna ab initio simulation package (VASP) [33]. The electron-ion interaction is described by the projector augmented wave (PAW) method [34]. The exchange and correlation functional adapts the Perdew-Burke-Ernzerhof (PBE) scheme [35]. Plane wave basis set with cutoff energy of 174 eV is used to ensure energy convergence, for both Gd and Ge. Surface energy is calculated via the slab model, in which a slab is sandwiched within a vacuum space to simulate the surface structure under periodic boundary conditions. The thicknesses of slab and of vacuum are chosen large enough to avoid interaction between two surfaces of the slab. For the pure elements, Ge(111) and Gd(0001) surfaces have densities ($N$) of 7.22 and 8.74 atoms nm$^{-2}$, respectively.

**Surface Energy of Ge(111).** The configuration of the valence states is $4s^24p^2$ for Ge. The optimized lattice constant is 0.5776 nm, close to the experimental value of 0.5658 nm [36]. Along the [111] direction, 9 bilayers are used to build the slab, with 1.473 nm of vacuum. Two bilayers on each side of the slab are fully relaxed, and the central 5 bilayers are fixed at the bulk positions. A $15\times15\times1\Gamma$-centered $k$-point sampling grid is used for the Brillouin zone integration. The surface energy is given by

$$E_{\text{surf}} = \frac{(E_{\text{tot, surf}} - E_{\text{tot, bulk}})}{2},$$

(1)

where $E_{\text{tot, surf}}$ is the total energy of the slab and $E_{\text{tot, bulk}}$ is the total energy of the bulk Ge with the same number of atoms. The factor of 2 reflects two identical surfaces in our calculation configuration. With this approach, the calculated surface energy of Ge(111) is 0.968 eV/atom, to be compared with the experimental value of 0.917 eV/atom [37].
**Surface Energy of Gd(0001).** For Gd, we treat $4f^7$ as part of the core electron configuration, and $5p^65d^16s^2$ as the valence configuration [38]. This electron configuration is reasonable since $4f^7$ electrons are strongly localized and play a negligible role in chemical bonding. The optimized lattice parameters are $a = 0.3632$ nm and $c/a = 1.575$, close to the experimental values of $a = 0.3636$ nm and $c/a = 1.590$ for Gd [39]. The surface structure of Gd(0001) is simulated by a slab with eight monolayers and 1.015 nm of vacuum along the [0001] direction. On each side of the slab, 2 monolayers are fully relaxed and the intermediate 4 are fixed at the bulk positions. The calculated surface energy of Gd(0001) is then 0.659 eV/atom, smaller than the experimentally-derived value of 0.79 eV/atom [40, 41], although it should be noted that the experimental value is not face-specific. The top surface layer shrinks inward by 2.6%, compatible with the experimental value of 3.5 ± 1.0% [42]. For comparison, other groups have calculated properties of Gd(0001) when $4f^7$ is included in the valence electron configuration. For instance, Bylander et al. [41] hybridized the Hartree-Fock and Local Spin-Density Approximation methods, and found that the surface energy of Gd(0001) was 0.824 eV/atom, with the top interlayer spacing contracted by 3.4%. Therefore, we conclude that PAW-PBE and $5p^65d^16s^2$ are reasonable choices for the computational method and valence electron configuration, respectively.

To summarize, our calculations show that the surface energy of Gd(0001) is 0.66 eV/atom, which is significantly less than that of Ge(111), 0.97 eV/atom, obtained by the same approach. In intermetallics, surfaces are usually dense planes that are richest in the low-surface-energy component. Our results therefore engender the expectation that preferred terminations of Gd$_5$Ge$_4$ should be those with high Gd content.
Surface Energies of Gd$_5$Ge$_4$ Terminations. With the same calculation configurations, the thermodynamic stability of the Gd$_5$Ge$_4$ surface along the [010] direction is theoretically investigated to clarify the STM observations in Section 3. The optimized lattice constants are $a = 0.7729$ nm, $b = 1.4852$ nm and $c = 0.7820$ nm for the $Pnma$ structure, close to the experimental values [11] $a = 0.770$ nm, $b = 1.483$ nm, and $c = 0.779$ nm, respectively.

We test four different layers as possible terminations. Two are the Gd layers labeled Gd$_1$ and Gd$_2$ in Fig. 1(A), with $N = 6.62$ atoms nm$^{-2}$. The third is the mixed layer, Gd-Ge$_1$ ($N = 9.93$ atoms nm$^{-2}$) and the fourth is a sparse Ge-termination, Ge$_2$ ($N = 3.31$ atoms nm$^{-2}$). A $7\times1\times7$ $\Gamma$-centered $k$-point sampling grid is used for the Brillouin zone integration for all surface configurations. The slab includes 18 atomic layers with a total of 40 Gd and 28 Ge atoms for Gd$_1$, 24 atomic layers with 48 Gd and 36 Ge atoms for Gd$_2$, 22 atomic layers with 40 Gd and 36 Ge atoms for Ge$_2$, and 16 atomic layers with 32 Gd and 28 Ge atoms for Gd-Ge$_1$ terminations, respectively. The vacuum space is 1.137 nm for the case of Gd$_2$, 1.836 nm for Gd$_1$, 1.464 nm for Ge$_2$ and 2.183 nm for Gd-Ge$_1$. Four layers on each side of the slab are fully relaxed and the central ones are fixed to the bulk positions, except for Gd$_1$ where the relaxation of three layers on the surface is sufficient for energy convergence.

Relaxation is most pronounced for the Ge$_2$ termination, where the separation between the top 2 planes of Ge atoms contracts from 0.131 nm in the bulk, to 0.075 nm. Because of this, we refer to the Ge-pure termination as Ge$_{2+3}$, with the inference that these two planes collapse into a single rumpled layer of Ge atoms ($N = 6.62$ atoms nm$^{-2}$).
The surface energy defined in Eq. (1) is not suitable for assessing the thermodynamic stability of the different terminations of Gd₅Ge₄, since cleavage of the bulk does not result in 2 identical surfaces. Instead, we adopt the method of Moll et al. [43] and define the surface energy per surface unit cell as

$$\frac{1}{2} E_{\text{surf}} = \frac{1}{2} \left( E_{\text{slab}} - n_{\text{Gd}} \times \mu_{\text{Gd}} - n_{\text{Ge}} \times \mu_{\text{Ge}} \right),$$

(2)

Here $E_{\text{slab}}$ is the total energy of the slab, $\mu_{\text{Gd}}$ (\(\mu_{\text{Ge}}\)) is the chemical potential of Gd (Ge) in Gd₅Ge₄, and $n_{\text{Gd}}$ ($n_{\text{Ge}}$) is the number of Gd (Ge) atoms in the slab. The factor of 2 results from the two identical terminations on each side of the slab used in the calculation. The chemical potential of Gd in the hcp phase (Ge in diamond phase) is defined as $\mu_{\text{Gd,Bulk}}$ ($\mu_{\text{Ge,Bulk}}$), and the chemical potential of Gd₅Ge₄ per unit cell (with 20 Gd and 16 Ge atoms per unit cell) as $\mu_{\text{Gd20Ge16}}^{\text{Bulk}}$. The relation $\mu_{\text{Gd20Ge16}}^{\text{Bulk}} = 20 \mu_{\text{Gd}} + 16 \mu_{\text{Ge}}$ is valid when there is thermal equilibrium between the surface and bulk region in Gd₅Ge₄. If $\mu_{\text{Gd}}$ is chosen as the independent variable in Eq. (2), then the surface energy can be rewritten as

$$\frac{1}{2} \left( E_{\text{surf}} - \frac{1}{2} n_{\text{slab}} \times \mu^{\text{Bulk}}_{\text{Gd20Ge16}} - 5 \times \mu^{\text{Bulk}}_{\text{Gd20Ge16}} \right).$$

(3)

The upper limit of $\mu_{\text{Gd}}$ is $\mu_{\text{Gd,Bulk}}$, since when $\mu_{\text{Gd}} = \mu_{\text{Gd,Bulk}}$, phase segregation will take place in Gd₅Ge₄. On the other hand, the formation energy of Gd₅Ge₄ per unit cell is defined as

$$\otimes H = 20 \mu_{\text{Gd}} + 16 \mu_{\text{Ge}} - \frac{\mu_{\text{Gd,Bulk}}}{2},$$

and the calculated value of $\otimes H$ is 30.916 eV/unit cell. Then the lower limit of $\mu_{\text{Gd}}$ must be $\mu_{\text{Gd,Bulk}} - \frac{\otimes H}{f}$. This is a manuscript of an article from Journal of Physics: Condensed Matter 25 (2013): 485002, doi: 10.1088/0953-8984/25/48/485002. Posted with permission.
20. From Eq. (3), the surface energy $E_{\text{surf}}$ can be evaluated for each of the four terminations as a function of $\mu_{\text{Gd}}$. 

The result is shown in Fig. 5. In the entire range of possible values of \( \mu_{\text{Gd}} \)

\[
(20 < \mu_{\text{Gd}} - \mu_{\text{Gd,Bulk}} < 0),
\]

one of the three terminations that contain Gd has the lowest \( E_{\text{surf}} \). The pure Ge termination is never favored. Thus, in the following discussion, we disregard Ge\(_{2+3}\) as a possible termination. In detail, the most stable surface configuration is the Gd-Ge\(_1\) termination when \( \mu_{\text{Gd}} - \mu_{\text{Gd,Bulk}} \) ranges from \( \infty H_f \) to -0.669 eV. It changes to Gd\(_2\) in the range -0.669 eV to -0.466 eV, and to Gd\(_1\) at -0.466 eV to 0 eV. In other words, this analysis shows that the preferred termination depends on the value of \( \mu_{\text{Gd}} \).

Our calculations also allow interpretation of the step heights between A and B-terranes. Table 1 gives average distances, \( D_{xy} \), between a top Gd-containing layer and the next 3 such layers for each of the three types of Gd-containing terminations. Separations between layers in the bulk structure are given for reference. Recall that from the STM data, the A-B or B-A step height is around 0.35 nm (0.31 to 0.39 nm). From the Table, this is compatible with the calculated distance \( D_{13} \) (0.405 nm) between Gd\(_1\) and Gd\(_2\), and with \( D_{12} \) (0.306 nm) between Gd\(_2\) and Gd\(_3\) (where Gd\(_3\) is equivalent to Gd\(_1\), as shown in Fig. 1(A)). However, the measured step heights are not consistent with other separations between Gd-containing layers. Therefore, we can reasonably deduce that if terraces A and B are bulk or bulk-like terminations, then they must correspond to Gd\(_1\) and Gd\(_2\), although we cannot say which is which.
Table 1. Average distance, $D_{xy}$, between the top layer ($x=1$) and deeper Gd-containing layers ($y$) for Gd$_1$, Gd$_2$ and Gd-Ge$_1$ terminations. The exact layers involved are specified in parentheses. The separation between bulk planes, from experiment [11], is given in square brackets for comparison.

<table>
<thead>
<tr>
<th>Termination</th>
<th>$D_{12}$, nm</th>
<th>$D_{13}$, nm</th>
<th>$D_{14}$, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd$_1$</td>
<td>0.202 (Gd$_1$-(Gd-Ge$_1$)) [0.210]</td>
<td>0.405 (Gd$_1$-Gd$_2$) [0.420]</td>
<td>0.729 (Gd$_1$-Gd$_3$) [0.740]</td>
</tr>
<tr>
<td>Gd$_2$</td>
<td>0.306 (Gd$_2$-Gd$_3$) [0.320]</td>
<td>0.518 (Gd$_2$-(Gd-Ge$_2$)) [0.530]</td>
<td>0.724 (Gd$_2$-Gd$_4$) [0.740]</td>
</tr>
<tr>
<td>Gd-Ge$_1$</td>
<td>0.230 ((Gd-Ge$_1$)-Gd$_2$) [0.210]</td>
<td>0.558 ((Gd-Ge$_1$)-Gd$_3$) [0.530]</td>
<td>0.765 ((Gd-Ge$_1$)-(Gd-Ge$_2$)) [0.740]</td>
</tr>
</tbody>
</table>

In addition, our analysis indicates that on the relaxed surfaces, the vertical displacement (rumpling) within a layer is as follows: 0.0014 nm between Gd atoms in Gd$_1$, 0.063 nm between Gd atoms in Gd$_2$, and 0.040 nm between Gd and Ge atoms in Gd-Ge$_1$ (Gd atoms higher than Ge atoms). This shows that the Gd$_1$ surface is much smoother than the other two. The smaller rumpling for Gd$_1$ vs. Gd$_2$ can be attributed to the layer beneath the surface, which is a flat dense Gd-Ge layer under the Gd$_1$ termination, but a sparse Ge layer under the Gd$_2$ termination. The circles in Fig. 1(B) represent Gd atoms in either Gd$_1$ or Gd$_2$. In this representation, Gd$_1$ and Gd$_2$ would differ only in the nature and arrangement of atoms in deeper planes.
Discussion.

The XPS data show that there is neither surface segregation nor preferential sputtering, within ± 5 at%. STM data show that step heights between equivalent terraces (A-A or B-B) are 0.75 ± 0.01 nm, which is half the bulk lattice parameter $b = 1.483$ nm. This is consistent with the existence of two mirror planes perpendicular to the $b$-axis and separated by half the $b$-axis length in the bulk unit cell. This indicates that the bulk structure vertical to the surface plane is maintained.

In Al-based intermetallics, surfaces are often bulk-terminated or closely related. (Here 'closely related' means, for instance, that surface deviations from bulk structure consist of missing atoms, or relaxed interlayer spacings.) The terminations are usually dense planes that are rich in the component having lowest elemental surface energy [44]. Based on the bulk structure of Gd$_5$Ge$_4$ and our DFT calculations, the possible (001) terminations are pure Gd (Gd$_1$ and Gd$_2$), pure Ge (Ge$_2$-3), and mixed composition (Gd-Ge$_1$). The relative densities of these terminations are 1.0, 1.0, and 1.5. Hence, densities increase in the order (pure Ge) = (pure Gd) < (Gd-Ge). However, our DFT calculations show that $E_{\text{surf}}$ for the close-packed surfaces of elemental Gd and Ge are 0.66 eV/atom and 0.97 eV/atom, so from this one might expect relative stabilities in Gd$_5$Ge$_4$ to increase in the order (pure Ge) < (Gd-Ge) < (pure Gd). Comparing the two trends shows that the pure Ge termination is not favored by either density or elemental surface energy, which is qualitatively consistent with the fact that it never has the lowest $E_{\text{surf}}$ in Gd$_5$Ge$_4$ (Fig. 5). On the other hand, for pure Gd and mixed Gd-Ge terminations there is a competition between density and elemental surface energy, qualitatively compatible with the fact that each of these terminations has lowest $E_{\text{surf}}$ in a different range of $\mu_{\text{Gd}}$ in Fig. 5.
In calculating $E_{\text{surf}}$ for different values of $\mu_{\text{Gd}}$, the range of $\mu_{\text{Gd}}$ is bounded by thermodynamic limits [45]. In other multicomponent systems, there is evidence that even slight differences in bulk composition and/or bulk defect density can shift the chemical potential within the allowed limits and stabilize different surface structures [46, 47]. Perhaps most striking is a series of studies of Al$_{13}$Co$_4$(100) [44, 48, 49], in which three different samples yielded three different surface structures, even though the surfaces were prepared in very similar fashion. Furthermore, the stability range of bulk Al$_{13}$Co$_4$ spans only 0.5 at%, so any differences in bulk composition must have been very small. Two of the samples were studied by STM, and the third by low-energy electron diffraction. The authors speculated that the apparent difference between surface structures could have been partly attributable to differences in the techniques applied [49]. However, even when comparing the two samples studied by the same technique—STM—surface structures were still clearly different. DFT confirmed that in the range of allowed chemical potential, several different surface structures were viable [44, 49].

For Gd$_5$Ge$_4$, DFT indicates that three possible terminations are viable, but the values of the step heights between A and B terraces are only consistent with the two Gd-pure terminations, not with the mixed Gd-Ge termination. (We omit the Ge-pure termination from consideration for reasons stated above.) The surface energies of these two Gd-pure terminations, Gd$_1$ and Gd$_2$, must be in close balance, since they co-exist on the surface. From the DFT results of Fig. 5, this condition is met when

$$\mu_{\text{Gd}} - \mu_{\text{Gd,bulk}} = -0.466 \text{ eV}.$$  

Then small variations in $\mu_{\text{Gd}} - \mu_{\text{Gd,bulk}}$ near this point could also explain the different predominance of A- vs. B-terraces on our two samples. Experimentally, our two samples differed in their history of preparation within UHV, one
having been subjected to more cycles of sputtering and annealing than the other, before the onset of STM experiments. We suggest that this sputter-annealing process may have led to a slightly different defect density and/or composition in the surface and near-surface region for one sample than the other, this in turn leading to small but significant differences in the chemical potential.

The foregoing discussion is based on the assumption that the surface structures are closely related to the bulk structure. This is reasonable, based on the XPS data, the step heights, and the observation of alternating terraces. However, in this study we have not identified lateral fine structure that confirms this hypothesis. Both types of terraces, A- and B-, contain many protrusions and depressions. The A-terraces also exhibit parallel stripes at an angle of 28° with the <001> direction in the surface plane [cf. Fig. 4(B)]. The long black lines in Fig. 1(B) show the two equivalent possible orientations of the stripes with respect to the (010) surface model; there is no simple relationship with the atomic structure. From STM, the stripes are 1.0 nm apart and 0.04 nm high. Hence, they are not very high relative to a typical atomic dimension (ca. 0.2 nm), and they are several times wider. At present, the origin of these stripes is not understood. They certainly indicate that the lateral bulk structure of Gd5Ge4 is not preserved exactly at the surface, although the perturbation could still be minor.

On the B-terraces, bumps are 0.31 to 0.40 nm tall, the same as the height between dissimilar planes. It is thus possible that the bumps represent small A-terrace-like regions. If this is the case, then they may be evidence of transient, metastable terraces that form during annealing. Small A-like bumps could result if either the A-terrace is replacing the B-terrace (bumps are growing and replacing the underlying terrace), or vice-versa.
(underlying B-terrace is replacing the bumps) at elevated temperature. Since the STM observations are made after the sample has cooled back to room temperature, they would be frozen in place as the sample cools. Hence, either the A- or B-terrace could be the less stable one. On quasicrystal surfaces, it is known that metastable terraces, or metastable regions within terraces, can form transiently during structural evolution at high temperature, and can leave their signature in the surface morphology when the sample is cooled for observation [50]. In Gd₅Ge₄(010), if one of the two terrace types (A or B) is transient, this could also contribute to the variability in the mix of A- and B-type terraces observed between the two samples studied with STM.

Conclusions.

The stability of the surface composition indicates that neither preferential sputtering nor surface segregation occurs on this surface, to within ±5 at%. After annealing above 900 K, STM reveals two types of terraces, which alternate laterally. Similar terraces are separated by a distance that is half the bulk unit cell. All of these observations can be explained by interpreting the surface structure in terms of the bulk structure. DFT calculations show that the surface energy of the close-packed plane of elemental Gd is lower than that of elemental Ge, which leads to a first-order expectation that surfaces of Gd₅Ge₄ are Gd-rich. This is borne out: Among the bulk terminations of Gd₅Ge₄, DFT shows that pure Ge terminations are not favored. The three remaining terminations (two pure Gd and one mixed Gd-Ge) are each favored in a different range of possible Gd chemical potential. DFT shows that step heights between dissimilar terraces
are consistent with the two pure Gd terminations. We postulate that the two observed terraces are closely related to the two pure Gd terminations. Small differences or variations in chemical potential may account for the fact that both terminations can co-exist, and for variations between two samples studied with STM.

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References.


[24] Samples were synthesized at the Materials Preparation Center, Ames Laboratory USDOE, Ames, IA, USA.: www.mpc.ameslab.gov


[28] www.CasaXPS.com


**Figure Captions.**

Fig. 1. The bulk structure of Gd₅Ge₄. Small circles are Ge atoms, and large circles are Gd atoms. The three colors for Gd (light blue, dark blue, and black—online) denote three sets of equivalent Gd atoms. (A) Two views of the bulk structure with the <010> (b-axis) in the plane of the paper. All atoms in, or intersected by, the unit cell are included. Atomic layers are labeled by a numerical subscript that denotes order of appearance, going from top to bottom. Dimensions are taken from Pecharsky and Gschneidner [11]. Mirror planes are shown by horizontal lines through Gd-Ge₁ and Gd-Ge₂. (B) View of the extended bulk structure perpendicular to the <010> direction. Only Gd atoms in a single layer are included. With reference to (A), this could be considered the Gd₁ layer or the Gd₂ layer. In (B), darker circles represent Gd atoms that are slightly higher than the other Gd atoms, representing the rumpling of this dense Gd layer. The rectangle shows the bulk unit cell. Solid lines show the orientation of surface stripes seen with STM.

Fig. 2. Atomic concentration of Gd measured with XPS. Horizontal dashed lines show the ideal bulk composition. (A) Surface composition as a function of annealing temperature. Symbol shapes indicate different samples: Diamonds for Sample #1, squares #2, triangles #3. Triangles filled with different shades represent different sets of measurements. (B) Surface compositions as a function of time during depth profiling, after annealing at different temperatures. All curves represent Sample #1 except for the 900 K data, which represent Sample #2.
Fig. 3. Illustration of A- and B-terraces. For all images, $V_{\text{tip}} = +1.0$ V, and $I = 0.5$ nA. (A) STM image showing that the two terrace types alternate in sequence. Image size is $100 \times 100$ nm$^2$. (B) B-terrace at high magnification. Image size is $34 \times 27$ nm$^2$. (C) Line profile defined by arrow in (B). (D) A-terrace at high magnification, showing the stripes. Image size is $33 \times 31$ nm$^2$. The $<100>$ and $<001>$ directions are shown above panel (D), and the line between these two vectors is parallel to the stripes. (E) Line profile defined by arrow in (D).

Fig. 4. STM images of surfaces under conditions where one type of terrace predominates. For all images, $V_{\text{tip}} = +1.0$ V, and $I = 0.5$ nA. (A) STM image after heating to 900 K. Image size is $250 \times 250$ nm$^2$. (B) STM image after heating to 1150 K. Image size is $100 \times 100$ nm$^2$. (C, D) STM images after heating to 900 K. Images are $250 \times 250$ nm$^2$. Circles denote regions where B-terraces protrude from step edges.

Fig. 5. (Color online) Surface energy of four surface layers as a function of $\mu_{\text{Gd}} - \mu_{\text{Gd,Bulk}}$, calculated from Eq. (3).
Fig. 1
Fig. 2
Fig. 3
Fig. 5