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Abstract

Gd oxidizes preferentially at the (0 1 0) surface of Gd_5Ge_4. This is consistent with thermodynamic data for the bulk oxides. Upon oxidation in vacuum, the gadolinium oxide displaces or covers the Ge. Oxidation is more extensive at 600 K than at 300 K, because more oxygen is incorporated into the surface and the shift of the Gd binding energy is larger.

Disciplines

Chemistry | Materials Science and Engineering

Preferential surface oxidation of Gd in Gd$_5$Ge$_4$

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ABSTRACT

Gd oxidizes preferentially at the (0 1 0) surface of Gd$_5$Ge$_4$. This is consistent with thermodynamic data for the bulk oxides. Upon oxidation in vacuum, the gadolinium oxide displaces or covers the Ge. Oxidation is more extensive at 600 K than at 300 K, because more oxygen is incorporated into the surface and the shift of the Gd binding energy is larger.

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1. Introduction

The Gd$_5$Si$_4$ and Gd$_5$Ge$_4$ binary systems [1], plus the pseudobinary Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ [2], were discovered in the 1960s by Smith et al. and Holtzberg et al., respectively. These systems are of interest because of their magnetic and thermomagnetic properties [3–5]. Giant magnetiocaloric effects were discovered in these systems in 1997 by Pecharsky and Gschneidner [6]. This and other properties such as giant magnetoresistance [7], spontaneous generation of voltage [8], metastability [9], and phase separation [10] may lead to new refrigeration and other energy conversion technologies.

Previous work has suggested that small amounts of interstitial oxygen can affect the coupled structural and magnetic phase transition in Gd$_5$Si$_2$Ge$_2$ [11]. Presumably, oxygen locks in the relative positions of loosely coupled, slab-like structural units in this type of compound. It has been postulated that oxygen has this effect because it occupies interstitial sites between the slabs. If this is correct, then oxygen would affect the magnetic transition temperature, and would reduce the magnetocaloric effect by eliminating the structural transition that often increases the total entropy change during the coupled magnetostructural transitions. Hence, it is important to understand the effect of oxygen in these systems.

Our primary focus here is on surface oxidation of the Gd$_5$Ge$_4$ phase. We choose the (0 1 0) surface because it is the closest-packed, meaning that it is likely to be the most stable surface. We

will show that Gd oxidizes preferentially at this surface and that the oxide covers or displaces Ge.

2. Materials and methods

We used a single crystal of Gd$_5$Ge$_4$, synthesized at the Materials Preparation Center of the Ames Laboratory [12], and cut to expose the (0 1 0) surface. X-ray photoelectron spectroscopy (XPS) experiments were performed with an Omicron X-ray source (Al Kα), and an Omicron EA 125 hemispherical electron energy analyzer. The XPS source was perpendicular to the sample plate, and the take-off angle (the angle between the entrance axis of the analyzer and the sample surface plane) was 45°. The angular acceptance range was ±8°. The aperture used in the EA 125 analyzer was 6 mm × 12 mm. The Gd 3d$_{5/2}$ peak, with a binding energy of 1186 eV, was chosen for analysis because it was most intense. The Ge 2p$_{1/2}$ peak, at 1248 eV, was chosen because it was the most intense peak that did not overlap with a Gd peak. (The Ge 2p$_{3/2}$, which is more commonly used for surface analysis, overlapped with the Gd 3d$_{3/2}$ peak.) XP spectra were analyzed with CasaXPS software [13]. The accuracy in determining binding energies, both for Gd and Ge was ±0.2 eV.

3. Results

After the Gd$_5$Ge$_4$ sample was initially placed in UHV, its composition was checked with XPS. This revealed carbon and oxygen contaminants. It was then sputtered at 300 K for several minutes. This process was repeated several times until there was no carbon detectable by XPS, and a small, invariant O 1s peak remained. (The source of the oxygen will be discussed below.) Fig. 1a shows the

Table 1
Measured binding energies of Gd $3d_{5/2}$ and Ge $2p_{1/2}$ under various conditions of surface preparation. Literature values are given for comparison.

| Peak	Surface condition	Measured binding energy (eV)	Literature values of pure metal and oxide
Gd $3d_{5/2}$	Cleaned by ion bombardment alone at 300 K	1186.1	
	Cleaned by ion bombardment, then annealing to 900 K	1186.2	
	Air-oxidized	1187.3	Pure Gd: 1186.0–1186.9 eV [15,16]
	Oxidized in UHV at 300 K	1187.0	Gd_2O_3: 1187.0–1189.5 eV [15]
	Oxidized in UHV at 600 K	1187.5	
Ge $2p_{1/2}$	Cleaned by ion bombardment alone at 300 K	1247.1	
	Cleaned by ion bombardment, then annealing to 900 K	1247.4	
	Air-oxidized	1247.5	Pure Ge: 1247.0–1248.2 eV [15]
	Oxidized in UHV at 300 K	No peak	GeO_2: 1250.6–1251.0 eV [17]
	Oxidized in UHV at 600 K	1248.2	

evolution of the Gd $3d_{5/2}$ peak, and Fig. 1b shows that of the Ge $2p_{1/2}$ peak, while the air-exposed sample was sputtered. The curves at the top are the contaminated surface, and those at the bottom are the clean surface. First, consider intensities. The intensity of the Gd peak decreases, and that of the Ge peak increases, as material is removed. Next, consider the peak positions (binding energies). The vertical dotted lines in Fig. 1 represent the initial (top) and final (bottom) positions of the Gd and Ge peaks. Initially, the Gd and Ge peaks are at binding energies of 1187.3 eV and 1247.5 eV. After 118 min of Ar^+ sputtering, they shift down to 1186.1 eV and 1247.1 eV, a change of −1.2 eV and −0.4 eV, respectively. The downward shift in binding energies can be explained by a transition from a more highly oxidized to a less oxidized surface. Key binding energies are summarized in Table 1.

In a separate set of experiments, the surface was annealed at 900 K to restore the surface atomic structure after ion bombardment. This did not change the intensity of the small residual oxygen peak at 531.1 ± 0.4 eV, which was present also after ion bombardment without annealing. It is apparent in the top curve of Fig. 2a. Its intensity corresponds to a concentration of 1.4 ± 0.7 at%. The constant presence and level of this residual oxygen, independent of sample treatment, suggests that a low level of oxygen is a bulk constituent.

After annealing, the sample was exposed to oxygen by backfilling the UHV chamber with O_2 at a pressure of 10^{-7} Torr for 1000 s. This equals an exposure of 100 Langmuir (L).

The sample was held at two temperatures, 300 K and 600 K, during oxygen exposure. The results for 300 K are shown in Fig. 2, and for 600 K in Fig. 3. In both figures, top curves represent the initial surface, and bottom curves represent the surface after oxygen exposure. Upon exposure to oxygen, the O 1s peak increases strongly and its binding energy shifts downward, to 529.8–530.0 eV, as shown in Figs. 2a and 3a. This indicates that oxygen adsorbs in both cases, i.e. the adsorption probability is substantial.
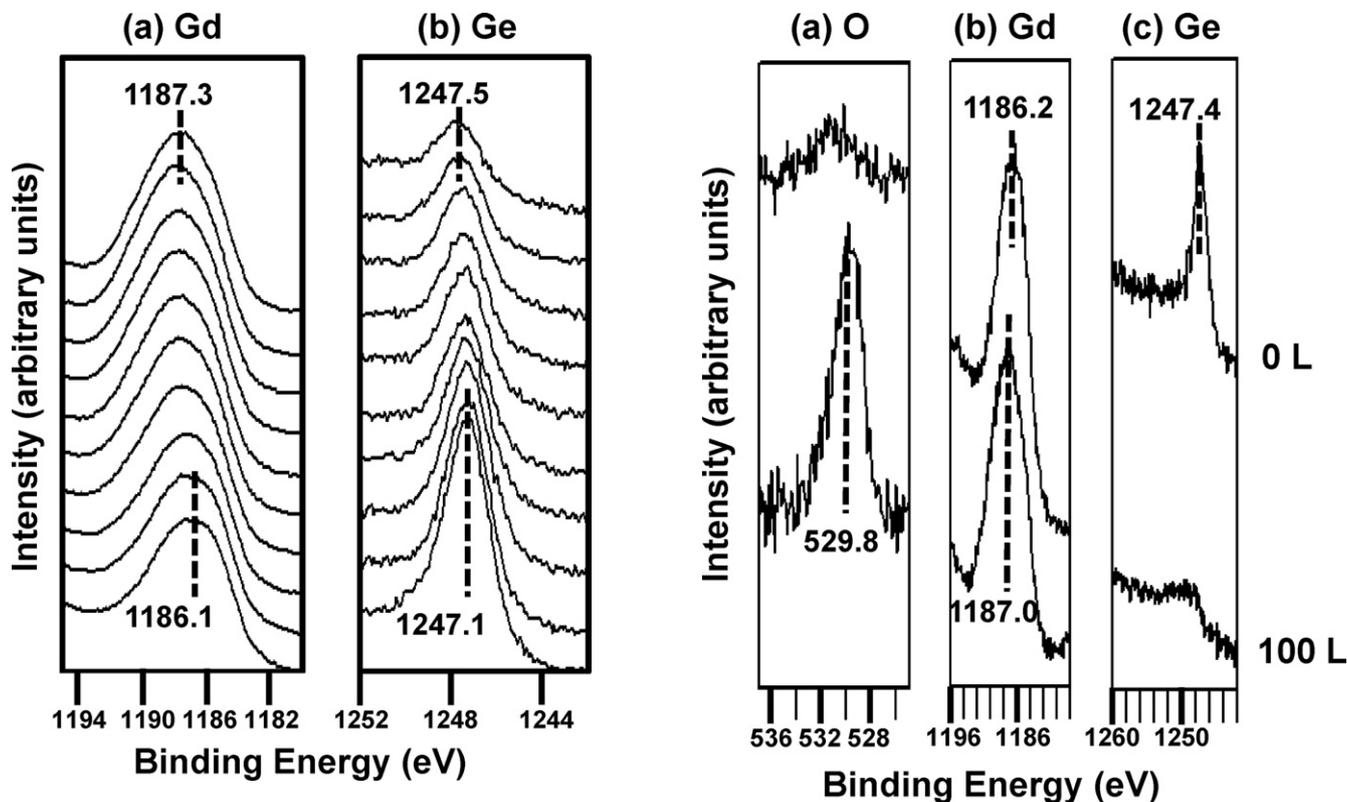
Fig. 1. X-ray photoelectron spectra showing (a) Gd $3d_{5/2}$ and (b) Ge $2p_{1/2}$ peaks after exposure to air at 300 K. The top curves represent the air-exposed surface, and bottom curves the clean surface. The dashed lines mark the initial and final peak positions. Curves are displaced vertically to avoid overlap.

Fig. 2. X-ray photoelectron spectra showing (a) O 1s, (b) Gd $3d_{5/2}$, and (c) Ge $2p_{1/2}$ peaks after 100 L of O_2 exposure within the UHV chamber at 300 K. Curves are displaced vertically to avoid overlap. The intensity scale is the same for all frames.
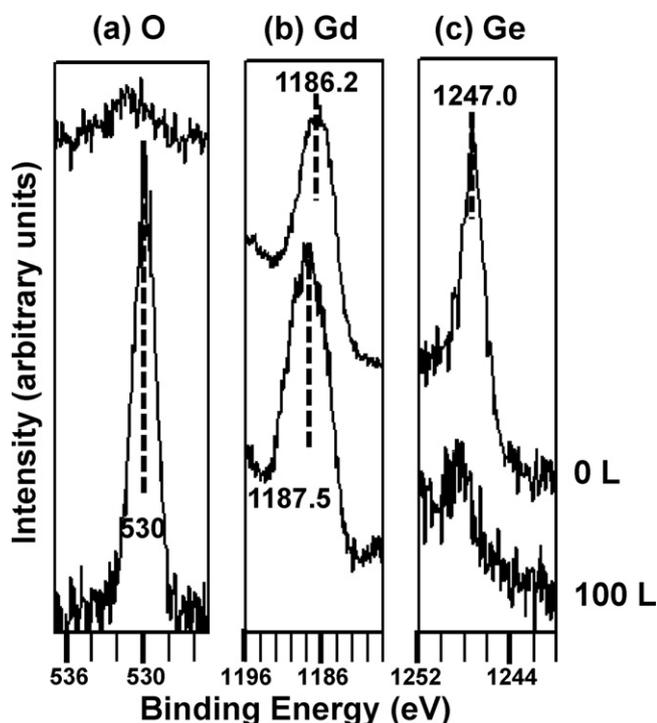
Fig. 3. X-ray photoelectron spectra showing (a) O 1s, (b) Gd $3d_{5/2}$, and (c) Ge $2p_{1/2}$ peaks after 100 L O_2 within the UHV chamber at 600 K. Curves are displaced vertically to avoid overlap. The intensity scale is the same for all frames.

4. Discussion

With regard to the Gd and Ge peak intensities, the oxygen adsorption experiments in Figs. 2 and 3 show the reverse of the trends during cleaning the air-oxidized surface as in Fig. 1. Adsorption of oxygen causes the Gd intensity to increase (slightly), and the Ge intensity to decrease. In fact, the Ge peak almost disappears after exposure to 100 L oxygen. It seems that Ge is displaced from the surface, or perhaps preferentially covered by oxygen, as a result of Gd oxidation.

Second, consider the shift in position of the Gd peak. The peak moves up in binding energy by 0.8 eV at 300 K—from 1186.2 eV to

1187.0 eV. Its binding energy also shifts upward, but by a larger amount (1.3 eV) at 600 K—from 1186.2 eV to 1187.5 eV. An upward shift in binding energy is typical for a metal when it oxidizes. The larger shift in the binding energy at 600 K than at 300 K supports the hypothesis that surface oxidation is enhanced at the higher temperature, correlating with a larger oxygen uptake.

To put the extent of oxidation on a more quantitative basis, we have deconvoluted the Gd $3d_{5/2}$ peak into a peak representative of the clean surface, and a peak representative of the oxidized state of Gd. This is shown in Fig. 4, where Fig. 4a shows the spectrum of the clean surface, Fig. 4b the oxidized surface at 300 K, and Fig. 4c the oxidized surface at 600 K. The position and width of the peak in Fig. 4a are used to fix the low-binding-energy component in the fitted spectra of Fig. 4b and c, at 1186.2 eV. The spectra in Fig. 4b and c are fit well by addition of a second component at higher binding energy, 1189.1 eV. Its relative intensity is higher after 600 K oxidation than after 300 K oxidation, confirming that oxidation is more extensive at higher temperature.

It is also informative to compare the absolute XPS peak positions with published values. The stable form of gadolinium oxide is Gd_2O_3 [14]. For this oxide, the Gd $3d_{5/2}$ binding energy is in the range 1187.0–1189.5 eV, according to the literature [15]. Our value for oxidized Gd is at 1189.1 eV, based upon peak-fitting. This is compatible. The energy range for clean elemental Gd is 1186.0–1186.9 eV [15,16]. Based upon peak-fitting, our value is 1186.2 eV, which is also compatible.

For Ge, the stable form of the bulk oxide is GeO_2 [14]. For this oxide, the Ge $2p_{1/2}$ binding energy is in the range 1250.6–1251.0 eV [15,17]. In the air-exposed sample, we find the Ge $2p_{1/2}$ peak at 1247.5 eV. This lies 3.1 eV outside the range expected for GeO_2. The measured value of the air-oxidized sample does, however, fall within the range for pure Ge, which is 1247.0–1248.2 eV [15]. After oxidation in vacuum, the Ge $2p_{1/2}$ peak is very small and its position is difficult to determine accurately, but it is still not compatible with GeO_2. Taken together, these observations indicate that Gd oxidizes but Ge does not.

Preferential oxidation of Gd in Gd_5Ge_4 is consistent with the hierarchy of enthalpies of formation of the bulk oxides of Gd and Ge. At room temperature, they are −1819.6 kJ/mol for Gd_2O_3, and −551.0 kJ/mol for GeO_2 [14]. Thus, preferential oxidation of Gd is thermodynamically driven.

A similar effect occurs at surfaces of three other rare earth alloys: $LaNi_5$ [18], UNi_2, and UNi_5 [19]. In those cases, as here, the rare
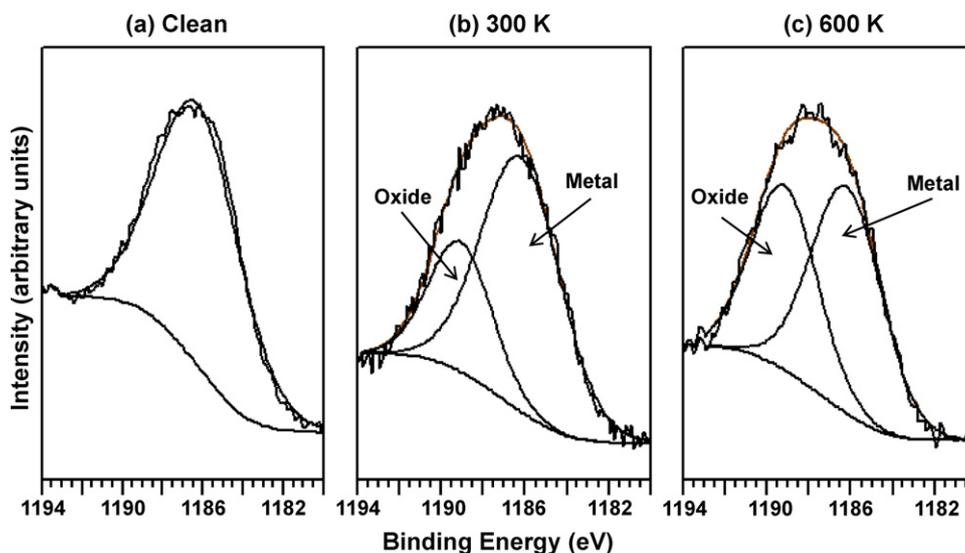
Fig. 4. Deconvoluted X-ray photoelectron spectra of Gd $3d_{5/2}$ peak showing the surface (a) after cleaning by ion bombardment and then annealing to 900 K, (b) after 100 L O_2 exposure at 300 K, and (c) after 100 L O_2 exposure at 600 K. The vertical intensity scale is the same for all frames.

earth oxidizes preferentially and the other component is effectively displaced from the surface. This phenomenon is driven by the well-known stability of the rare earth oxides.

5. Conclusions

We have found that Gd undergoes preferential oxidation at the $(0\,1\,0)$ surface of Gd_5Ge_4. This is consistent with thermodynamic data for the bulk oxides. Upon oxidation in vacuum, the gadolinium oxide displaces or covers the Ge. Oxidation in vacuum is more extensive at 600 K than at 300 K, based upon the observation that more oxygen is incorporated into the surface and the shift of the Gd binding energy is larger. A small amount of oxygen (about 1.4 at.%) is a bulk constituent in this sample.

Acknowledgments

References

[1] G.S. Smith, A.G. Tharp, W. Johnson, Rare earth-germanium and -silicon compounds at 5:4 and 5:3 compositions, Acta Crystallogr. 22 (1967) 940–943.
[2] F. Holtzberg, R.J. Gambino, T.R. McGuire, New ferromagnetic 5:4 compounds in the rare earth silicon and germanium systems, J. Phys. Chem. Solids 28 (1967) 2283–2289.
[3] D. Paudyal, V.K. Pecharsky, K.A. Gschneidner, B.N. Harmon, Magnetism of Gd_5Ge_4 from first principles, Phys. Rev. B: Condens. Matter 75 (2007) 094427.
[4] D. Paudyal, V.K. Pecharsky, K.A. Gschneidner, Origins of ferromagnetism and antiferromagnetism in Gd_5Ge_4, J. Phys.: Condens. Matter 20 (2008) 235235.
[5] J.D. Moore, G.K. Perkins, Y. Bugoslavsky, M.K. Chattopadhyay, S.B. Roy, P. Chaddah, V.K. Pecharsky, K.A. Gschneidner, L.F. Cohen, Reducing the operational magnetic field in the prototype magnetocaloric system Gd5Ge4 by approaching the single cluster size limit, Appl. Phys. Lett. 88 (2006) 072501.
[6] V.K. Pecharsky, J.K.A. Gschneidner, Giant magnetocaloric effect in Gd5(Si_2Ge_2), Phys. Rev. Lett. 78 (1997) 4494–4497.
[7] L. Morellon, J. Stankiewicz, B. Garcia-Landa, P.A. Algarabel, M.R. Ibarra, Giant magnetoresistance near the magnetostructural transition in Gd5(Si1.8Ge2.2), Appl. Phys. Lett. 73 (1998) 3462–3464.
[8] E.M. Levin, V.K. Pecharsky, K.A. Gschneidner, Spontaneous generation of voltage in Gd5(SixGe{4-x}) during a first-order phase transition induced by temperature or magnetic field, Phys. Rev. B: Condens. Matter 63 (2001) 174110.
[9] M.K. Chattopadhyay, M.A. Manekar, A.O. Pecharsky, V.K. Pecharsky, K.A. Gschneidner, J. Moore, G.K. Perkins, Y.V. Bugoslavsky, S.B. Roy, P. Chaddah, L.F. Cohen, Metastable magnetic response across the antiferromagnetic to ferromagnetic transition in Gd5Ge4, Phys. Rev. B: Condens. Matter 70 (2004) 214421.
[10] V.K. Pecharsky, A.P. Holm, K.A. Gschneidner, R. Rink, Massive magnetic-field-induced structural transformation in Gd5Ge4 and the nature of the giant magnetocaloric effect, Phys. Rev. Lett. 91 (2003) 197204.
[11] Y. Mozharivskyj, A.O. Pecharsky, V.K. Pecharsky, G.J. Miller, On the high-temperature phase transition of Gd5Si2Ge2, J. Am. Chem. Soc. 127 (2005) 317–324.
[12] Samples were synthesized at the Materials Preparation Center, Ames Laboratory USDOE, Ames, IA, USA. See: www.mpc.ameslab.gov.
[13] See www.CasaXPS.com.
[14] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney, R.L. Nuttall, The NBS Tables of Chemical Thermodynamic Properties: Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units, American Chemical Society and American Institute of Physics, Washington, DC, 1982.
[15] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data, Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie, MN, 1992.
[16] C.J. Powell, A. Jablonski, NIST Electron Effective-Attenuation-Length Database-Version 1.3, National Institute of Standards and Technology, Gaithersburg, MD, 2011.
[17] I. Lucy, J. Beynon, B. Orton, X-ray photoelectron spectra of Cu–GeO2 thin films prepared by vacuum co-evaporation, J. Mater. Sci. Lett. 16 (1997) 1477–1479.
[18] H.C. Siegmann, L. Schlapbach, C.R. Brundle, Self-restoring of the active surface in the hydrogen sponge LaNi5, Phys. Rev. Lett. 40 (1978) 972–975.
[19] T. Gouder, C.A. Colmenares, J.R. Naegele, J.C. Spirlet, J. Verbist, A surface spectroscopy study of the oxidation properties of UNi2 and UNi5, Surf. Sci. 265 (1992) 175–186.