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# The chemistry of the gadolinium–nickel interface

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Gadolinium overlayers on Ni(111) have been studied by angle resolved photoemission, angle resolved AES, LEED, and RHEED. We have observed pronounced interdiffusion of nickel with the gadolinium overlayer at temperatures as low as 150 K. This is in marked contrast with gadolinium overlayers on Cu(100) where substantial interdiffusion is not observed until 360 K, but is consistent with studies of ytterbium on nickel. [A. Nilsson, B Eriksson, N. Martensson, J. N. Andersen, and J. Onsgaard, *Phys. Rev. B* **38**, 10357, (1988) and I. Chorkendorff, J. Onsgaard, J. Schmidt–May and R. Nyholm, *Surf. Sci.* **160**, 587, (1985).] There is a strong interfacial heat of interaction observed with gadolinium on both copper and nickel resulting in pronounced binding energy shifts observed in photoemission. An extremely small kinetic barrier to rare earth diffusion through nickel has been measured. The results are compared to transition metal overlayers on transition metal substrates.

## I. INTRODUCTION

The interaction of metal overlayers with metal substrates is an area of widespread interest.<sup>1</sup> For magnetic overlayers, the chemical interaction of the overlayer with the substrate is important because of the influence the substrate may exert on the magnetic properties of the overlayer.<sup>2,3</sup> For transition metal overlayers on transition metal substrates, interdiffusion commonly occurs only at temperatures above 500 K.<sup>4,5</sup> For rare earth overlayers, interdiffusion has been observed at much lower temperatures.<sup>6–8</sup> The driving force for this has been postulated to be a large interfacial heat of formation.<sup>7</sup> We have observed very rapid interdiffusion of Gd overlayers on Ni(111), compared to transition metal overlayers, at temperatures as low as 150 K. We have also measured the kinetic barrier to Gd diffusion and found a correspondingly small value.

## II. EXPERIMENTAL

In order to study the magnetic properties of ferromagnetic overlayers on ferromagnetic substrates, we deposited Gd on Ni(111) single crystals. To properly characterize the interface, we performed low energy electron diffraction (LEED), reflection high energy electron diffraction (RHEED), angle and temperature dependent Auger electron spectroscopy (AES), and angle-resolved ultraviolet photoemission spectroscopy (ARUPS) experiments.

The Gd was evaporated from slugs of 99.9% purity in resistively heated W baskets. The baskets were precleaned by annealing to above the Gd melting point before loading the source. Water and liquid nitrogen cooling of the source allowed evaporations to be done with a base pressure increase of at most  $2\text{--}3 \times 10^{-10}$  Torr. Typically, 6–10 evaporations were done from a well outgassed source before the actual experiments were done. AES indicated the films were uncontaminated within the sensitivity of our spectrometer.

The films were evaporated onto clean, well-ordered Ni(111) surfaces at temperatures between 150–500 K as de-

termined by a chromel–alumel (type K) thermocouple. Films ranging from submonolayer to 200 Å coverages were grown. The thickness was monitored with an oscillating quartz crystal monitor. Since there was a large amount of interdiffusion occurring, the state coverages should be considered a relative guide to the amount of Gd deposited. We estimate our coverages accurate to 20%.

The AES and RHEED experiments were done in a chamber equipped with a Leybold-Heraeus EA-10 hemispherical analyzer and a home-built RHEED system. The spectrometer has an angular resolution of 4°. The base pressure of the chamber was typically  $5\text{--}6 \times 10^{-11}$  Torr. The LEED and ARUPS experiments were carried out in a separate vacuum chamber with a base pressure of  $1\text{--}2 \times 10^{-10}$  Torr. The photoemission experiments were done on two separate 6 m toroidal grating monochromators (TGMs) at the 1 GeV ring at the Synchrotron Radiation Center in Stoughton, Wisconsin. The combined monochromator and electron energy analyzer resolution varied from 0.15 to 0.3 eV.

## III. RESULTS

We used RHEED in conjunction with our LEED system to try and determine the overlayer structure. Our results were inconclusive. After depositing Gd onto well-ordered surfaces, we were unable to observe any significant surface structures with enough long range order to produce a RHEED or LEED pattern. Only diffuse scattering was observed. The exception to this being for approximately 1 monolayer (ML) coverage, we were able to observe a RHEED pattern after annealing the film to 600 K. The RHEED pattern was again similar to the original Ni(111) pattern and AES of the annealed film showed no detectable Gd signal. This indicated that the Gd had diffused into the crystal.

To determine if the lack of overlayer order was due to a lattice mismatch between hcp Gd (basal plane = 3.64 Å, *c/a* ratio = 1.588) and fcc Ni(111) (3.52 Å), or interdiffusion of Gd and Ni, we carried out angle resolved AES studies.<sup>9</sup>

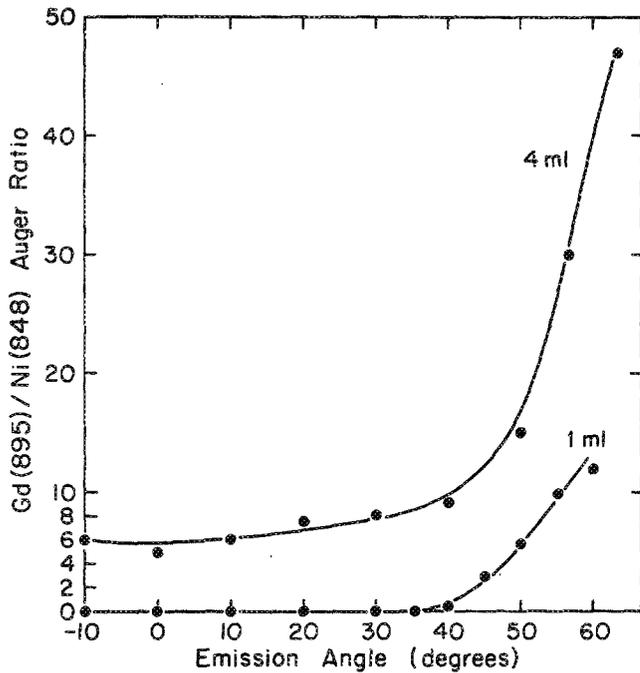


FIG. 1. Results from angle resolved AES. The Gd(895 eV)/Ni(848 eV) Auger signal intensity is plotted as a function of emission angle. Normal emission is 0°. The intensity ratio has been corrected for cross section. (Ref. 10). Data for 1 and 4 ML films at 300 K are shown. Films as low as 150 K exhibit a similar behavior.

Representative results are shown in Fig. 1. This figure shows the Gd 895 eV to Ni 848 eV Auger electron intensity ratios as a function of emission angle. The ratios were corrected for cross sections and the nearly identical kinetic energy of the electrons means the electron escape depth is about the same.<sup>10</sup> These films were deposited at 300 K, but the films at

150 K showed the same type of behavior. Notice that the ratio of Gd to Ni is nearly constant with emission angle until large angles of 40° off normal are reached.

We also did temperature-dependent AES to measure the kinetic activation barrier to diffusion. If we write down a simple Arrhenius expression for the diffusion rate  $R$ ,

$$R = De^{-E_d/kT}, \quad (1)$$

then by measuring the time rate of change of the Auger intensity ratio as a function of temperature and at constant coverage, we can determine the activation barrier  $E_d$ .<sup>11</sup> Our results for a constant coverage of nominally 4 Å ML thick films are shown in Fig. 2. Plotted is the logarithm of the time rate of change of the Gd to Ni signal versus the inverse temperature. The data were taken over a time scale ranging from 2 to 480 min. The Arrhenius expression, Eq. (1), shows that the slope gives the activation barrier. A linear least squares fit to the data yields  $E_d = 0.047 \pm 0.015 \pm 0.010$  eV. This surprisingly small value is consistent with interdiffusion at 150 K and is partly responsible for the large scatter in the data.

Since it is possible to relate core-level shifts with thermochemical quantities, we measured with photoemission the binding energy shifts of the Ni 3*p* and the Gd 4*f* levels as a function of coverage.<sup>12</sup> The results are shown in Fig. 3. Results from previous work of Gd on Cu(100) are also shown for reference.<sup>7</sup> The Ni 3*p* levels shift by 0.65 eV to higher binding energy with all but 0.05 eV shift coming with submonolayer coverages. On Ni(111), the Gd 4*f* levels shift 0.2 eV to lower binding energy. Notice that the Gd levels shift very little from 1–4 ML, it is not until higher coverages, greater than 4 ML, before the bulk binding energy of 8.4 eV is reached.<sup>13</sup> On Cu(100), the 4*f* levels shift 0.45 eV to lower binding energy as well, but they shift continuously with increasing coverage until reaching the bulk binding energy at 3–4 ML.

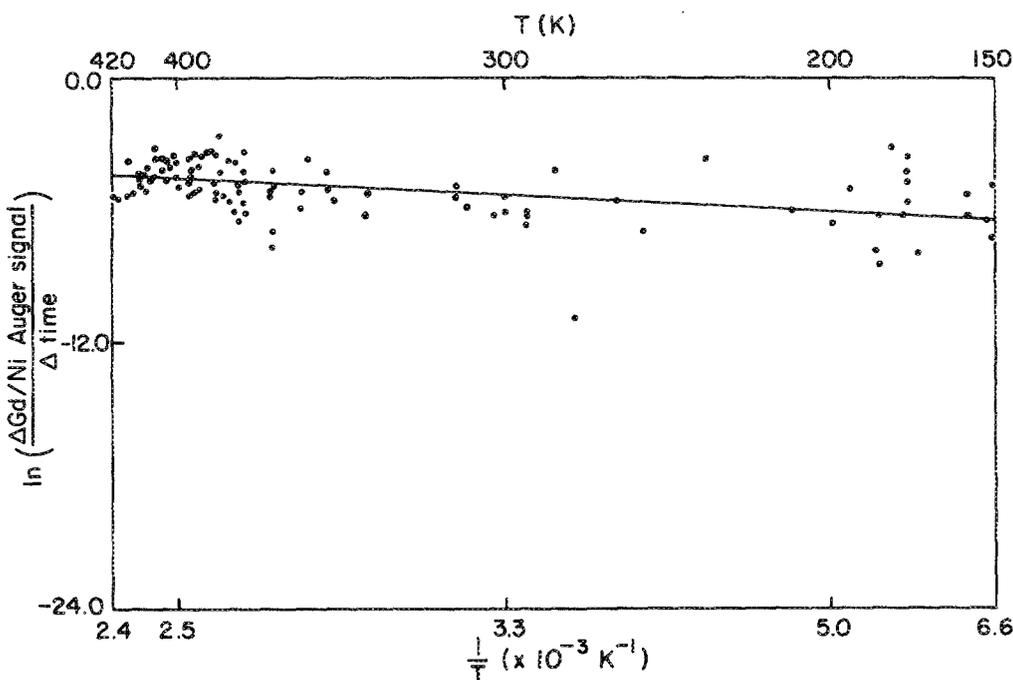


FIG. 2. Shown here is a temperature-dependent study of the diffusion activation barrier. The  $\ln$  time rate of change of the Gd(895 eV) to Ni(848 eV) Auger signal is plotted against the inverse temperature. The straight line is a linear least squares fit to the data. The slope gives the activation barrier to be  $0.047 \pm 0.015 \pm 0.010$  eV. The data were taken on constant coverage films of nominally 4 ML thickness.

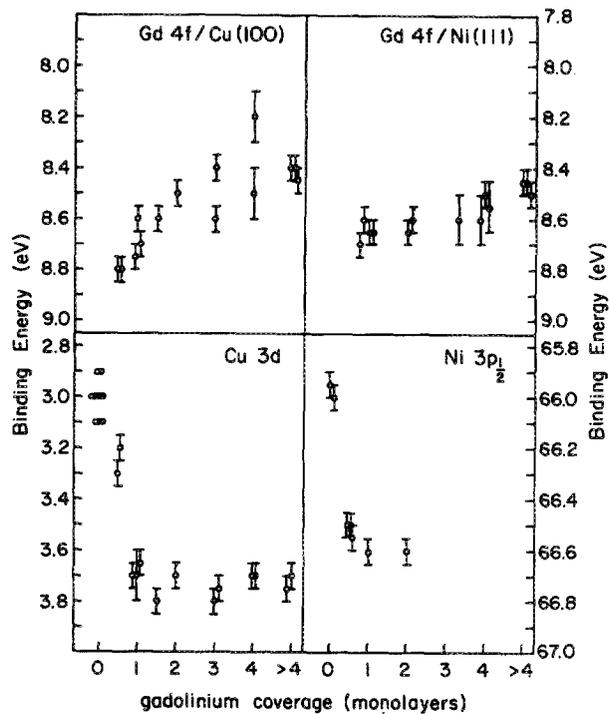


FIG. 3. These charts show the binding energy shifts of the Gd 4*f*, Cu 3*d*, and Ni 3*p* levels as a function of Gd coverage derived from photoemission data. The binding energies are referenced to the Fermi energy.

It is also noteworthy that we tried to measure the Gd 4*f* levels at lower coverages on Ni(111) than are plotted in Fig. 3, but the Gd diffused into the substrate so rapidly that within 5 min no Gd signal could be measured. This is shown in Fig. 4, which demonstrates the effect of 20 min on the pho-

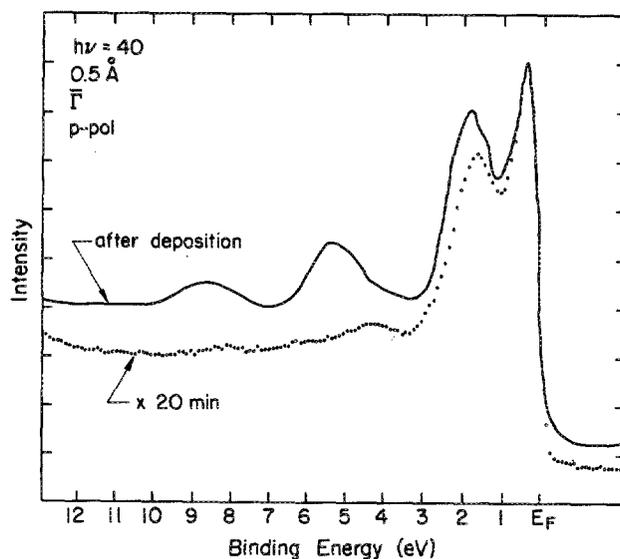


FIG. 4. Valence band energy distribution curves for approximately 1/4 ml of Gd at room temperature. The two spectra are just after deposition and after 20 min. The features at 8.5, 5.7, and partially at 1.7 eV are Gd derived.

toemission spectra from a submonolayer film at room temperature.

Figure 5 shows the valence band photoemission spectra of an 8 ml film at 150 K. The photoemission features are the Gd 4*f* levels at 8.5 eV binding energy, a strong satellite at 5.7 eV, and the Gd and Ni *d* bands at 1.7 eV and  $E_F$ . The two features nearest  $E_F$  are indicative of alloying, possibly multiphased, as will be discussed in more detail later. As an aside, the feature at 5.7 eV is seen at most Gd coverages, even in 200 Å thick films which in all other respects look like bulk Gd, i.e., no detectable Ni signal. In submonolayer coverages, its oscillator strength is suppressed. The origin of this feature is not clear, but contamination has been ruled out. We believe it to be an interband loss feature due to excitations from the *d* band to the unoccupied 4*f* levels.<sup>14</sup>

#### IV. DISCUSSION

The results we have obtained clearly indicate extensive alloying occurs at the Gd, Ni interface. As shown in Fig. 1, the Gd to Ni Auger ratio as a function of emission angle is nearly constant out to 40° off normal where it rises rapidly. Geometrical arguments would indicate that if the interface was abrupt and the films were growing in layers, then a  $1/\cos \phi$  dependence would be expected. The AES data allow us to rule out this possibility. The behavior of the Auger data can be explained in one of two ways. Either we have some type of island growth occurring or we have an interfacial alloy. Since Gd is a metal of lower surface free energy than Ni, thermodynamic arguments would favor Gd wetting the Ni surface rather than forming islands.<sup>15</sup> This idea, combined with our photoemission and temperature-dependent AES data, allow us to rule out island growth as an explanation. The relatively sharp increase in the Auger intensity ratios at large angles could be an indication of a surface segregation effect possibly driven by the larger atomic size of Gd atoms compared to Ni.

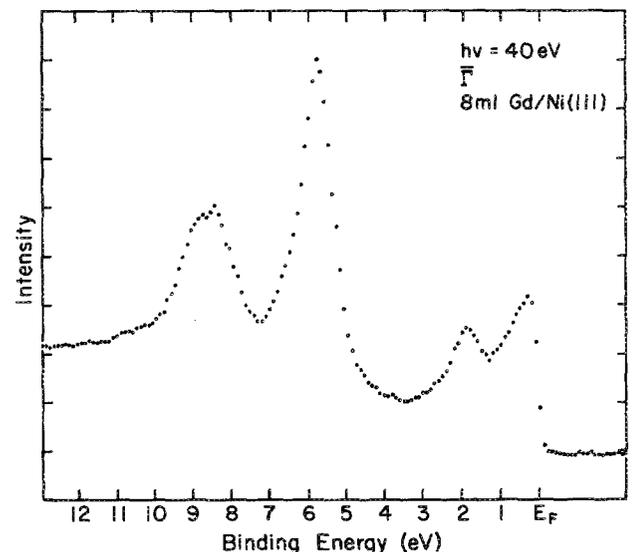


FIG. 5. This is the photoemission valence band energy distribution curve for 8 ml (32 Å) of Gd on Ni(111). The features are the Gd 4*f* levels at 8.5 eV, a satellite at 5.7 eV, and the hybridized Gd/Ni *d* bands at 1.7 eV and  $E_F$ .

The photoemission structure of the Gd, Ni  $d$  bands are a strong indication against island growth. If island growth was occurring, we would expect the photoemission spectra to resemble bulk Gd, especially at higher coverages. This is not what we observe. We observe a hybridization of the Ni and Gd  $d$  bands in films up to 32 Å thick, as in Fig. 5. The occupied Gd  $d$  band has previously been shown to be of  $d_{3z^2-r^2}$  atomic character.<sup>16</sup> This can mix [in a linear combination of atomic orbitals (LCAO) approximation] with the bottom of the Ni conduction band which also has  $d_{3z^2-r^2}$  character.<sup>17</sup> The result would be an increase in the density of states at the bottom of the Ni conduction band on Gd deposition, as we have observed. For island growth, a coverage of 32 Å should obscure any Ni derived features or have thick patches more representative of bulk Gd.

Further evidence in favor of alloy formation are the Ni 3*p* core level shifts (Fig. 3). We observe a chemical shift of  $0.65 \pm 0.05$  eV at 150 K. The surface core level shift (SCLS) for Ni(111) has been calculated to be 0.29 eV to lower binding energy.<sup>18</sup> The SCLS could then explain only 0.29 of the 0.65 eV shift. Island growth would imply an even smaller contribution to the 0.65 eV shift from the SCLS since not all the Ni surface atoms would be covered by Gd. (The SCLS is primarily a function of coordination number, not chemical environment.)<sup>12</sup> There would still be a significant photoemission oscillator strength from these exposed Ni atoms until the Gd islands grew large enough to cover the entire surface. However, we observe almost the entire Ni 3*p* shift at submonolayer coverage. What can explain the core level shift is a large interfacial heat of formation. Heats of formation have been shown to be directly related to core level binding energy shifts.<sup>19</sup> Our data show this heat to be at least 0.36 eV/atom (0.65–0.29 eV).

The different behavior of the Gd 4*f* level shifts with coverage on Cu(100) versus Ni(111) is a consequence of alloying at the Ni interface. Previous work has shown that Gd on Cu(100) has an abrupt interface up to 360 K.<sup>7</sup> On Cu, the 4*f* levels shift gradually from 8.8 to 8.4 eV on increasing coverage from 0.5 to 4 ML. This is consistent with the measured Gd SCLS of 0.48 eV.<sup>13</sup> On the other hand, for Gd on Ni(111) the 4*f* levels shift by only 0.1 eV at 4 ml. It is not until higher coverages that the bulk Gd value of 8.4 eV is reached. This is what would be expected from Gd diffusing into a Ni matrix. The lower coverages of Gd would have all the Gd atoms in a roughly similar environment as a result of alloying.

Additional strong evidence for rapid diffusion comes from the disappearance of the Gd photoemission signal (Fig. 4). Submonolayer coverages of Gd were deposited at room temperature and a spectrum showing Gd features was taken. Within 20 min, without changing the sample position, no Gd signal could be detected. Given the low vapor pressure of Gd, this result can only be explained by the dissolution of Gd into the Ni into such low concentrations that it was no longer detectable.

What is really surprising about rare earth systems is the extent of alloying even at low temperatures. For a typical transition metal overlayer on a transition metal substrate, interdiffusion does not become a problem until temperatures

around 500 K.<sup>4,5</sup> For the rare earths Sm, Yb, and Gd, the onset of interdiffusion and alloying are observed from 150 to 300 K.<sup>6–8</sup>

To understand this behavior, we need to remember that there are two important aspects driving diffusion. The first is the thermodynamical advantage of lowering the Gibb's free energy of the system. The alloy is frequently a system of lower free energy because the alloy can support a much larger entropy term. Previous researchers have measured the heat of formation of Gd–Ni alloys.<sup>20,21</sup> They find that the maximum value is about 0.4 eV/atom (this is a concentration dependent value). This is consistent with our Ni 3*p* core level shift derived value of 0.36 eV. This value is a factor of two larger than heats of formation of typical transition metal–transition metal alloys.<sup>22</sup> Clearly there is a strong driving force for alloy formation.

An alloy state of lower free energy is not the only requirement for rapid interdiffusion to occur. The other aspect to diffusion is the kinetic activation behavior. As shown in Fig. 2, we have measured this barrier to be about  $0.047 \pm 0.015 \pm 0.010$  eV. This is an order of magnitude smaller than activation barriers for transition metals to diffuse through transition metals.<sup>23</sup>

Although seemingly surprising, this small activation barrier can be understood. The kinetic process of diffusion is essentially a combination of the ionic vibration about its equilibrium position, i.e., the Debye–Waller factor  $W$ ; the potential energy barrier between sites, and the resulting tunneling probabilities.<sup>23</sup> The Debye–Waller factor is a measure of the mean square displacement of the ion compared to a lattice spacing. This is proportional to the inverse square of the Debye temperature,  $\Theta_D$ , for any solid ( $W \sim \Theta_D^{-2}$ ).<sup>24</sup> At 298 K, the Debye temperature of Gd is 155 K.<sup>25</sup> The transition metals have typically much higher Debye temperatures. Nickel for example has a Debye temperature of 345 K at 298 K.<sup>25</sup> The smaller Debye temperature means a larger Debye–Waller factor and hence larger diffusion rate. This is consistent with our measured value and observed interdiffusion at reduced temperatures compared to transition metals. The small Debye temperature is characteristic of all the rare earths and not just Gd.<sup>25</sup> The physical origins of the lower Debye temperatures are the large mass differences between the rare earths and transition metals ( $\Theta_D \sim M^{-1/2}$ ), and the smaller spring constant in the rare earth harmonic crystal as compared to typical transition metals.

As mentioned earlier, prior work on Gd on Cu(100) showed that interdiffusion did not begin until 360 K.<sup>7</sup> The temperature difference between Ni and Cu is easily explained. A simple Miadema calculation of the heats of formation for Gd/Ni alloys and Gd/Cu alloys yields 0.38 and 0.25 eV/atom, respectively.<sup>22</sup> The smaller heat for Cu means a smaller driving force than for Gd in Ni. The activation barrier for Gd diffusion through Cu has not been measured by us.

## V. CONCLUSIONS

We have observed the interdiffusion of Gd overlayers on Ni(111) single crystals at temperatures as low as 150 K. We have measured the interfacial heat of formation to be at least

0.36 eV/atom. The kinetic activation barrier is very small at  $0.047 \pm 0.015 \pm 0.010$  eV. This combination of a large interfacial heat of formation and a small kinetic barrier leads to rapid interdiffusion of rare earth overlayers on transition metal substrates at temperatures significantly lower than for transition metal overlayers. With the growing interest in low-dimensional magnetic systems and the varied magnetic properties of the rare earths, it is important for researchers to understand the chemistry of the rare earth, transition metal interface before drawing conclusions about their magnetic properties.

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<sup>1</sup>For a recent review and references, see P. A. Dowben, M. Onellion, and Y. J. Kime, *Scanning Microsc.* **2**, 177 (1988).

<sup>2</sup>C. L. Fu, A. J. Freeman, and T. Oguchi, *Phys. Rev. B* **54**, 2700 (1985).

<sup>3</sup>C. Carbone and E. Kisker, *Phys. Rev. B* **36**, 1280 (1987).

<sup>4</sup>J. Mazaruski and P. A. Dowben, in *Surface Science and Related Phenomenon*, edited by P. A. Dowben and A. Miller (Chemical Rubber, Cleveland, OH, 1989).

<sup>5</sup>P. A. Dowben, D. Wright, and M. Grunze, *Surf. Sci.* **134**, 1524 (1983).

<sup>6</sup>D. M. Wieliczka and C. G. Olson, *J. Vac. Sci. Technol. A* **8**, 891 (1990).

<sup>7</sup>D. LaGraffe, P. A. Dowben, and M. Onellion, *Phys. Rev. B* **40**, 3348 (1989).

<sup>8</sup>A. Nilsson, B. Eriksson, N. Martinsson, J. N. Andersen, and J. Onsgaard, *Phys. Rev. B* **38**, 10357 (1988).

<sup>9</sup>N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College, Philadelphia, 1976).

<sup>10</sup>L. E. Davis, N. C. MacDonald, P. W. Palmberg, G. E. Riach, and R. E. Weber, *Handbook of Auger Electron Spectroscopy* (Perkin-Elmer, Eden Prairie, MN, 1976).

<sup>11</sup>S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1941).

<sup>12</sup>For an excellent review of core level shifts, see W. F. Egelhoff, Jr., *Surf. Sci. Rept.* **6**, 253 (1987).

<sup>13</sup>R. Kammerer, J. Barth, F. Gerken, A. Flodstrom, and L. I. Johansson, *Solid State Commun.* **41**, 435 (1982).

<sup>14</sup>D. LaGraffe, P. A. Dowben, and M. Onellion (in preparation).

<sup>15</sup>This is based upon empirical correlations shown between the surface energy and the average electronic density ( $\sigma \sim r_s^{-5/2}$ ), where  $r_s$  is the classical conduction electron volume. See, R. A. Craig, *Phys. Rev. B* **6**, 1134 (1972); J. Schmidt and A. A. Lucas *Solid State Commun.* **11**, 415 (1972).

<sup>16</sup>D. LaGraffe, P. A. Dowben, and M. Onellion, *Phys. Rev. B* **40**, 970 (1989).

<sup>17</sup>F. J. Himpsel, J. A. Knapp, and D. E. Eastman, *Phys. Rev. B* **19**, 2919 (1979).

<sup>18</sup>P. H. Citrin and G. K. Wertheim, *Phys. Rev. B* **27**, 3176 (1983).

<sup>19</sup>P. Oelhafen, *J. Phys. F* **11**, L41 (1981).

<sup>20</sup>C. Colinet, A. Pasturel, and K. H. J. Buschow, *J. Appl. Phys.* **62**, 3712 (1987).

<sup>21</sup>C. Colinet, A. Pasturel, and K. H. J. Buschow, *Metall. Trans.* **17A**, 777 (1986).

<sup>22</sup>A. R. Miadema, P. F. Chatel, and F. R. de Boer, *Physica (Utrecht)* **100B**, 1 (1980).

<sup>23</sup>P. G. Shewmon, *Diffusion in Solids* (McGraw-Hill, New York, 1960).

<sup>24</sup>J. Ziman, *Theory of Solids* (Cambridge University, Cambridge, 1971).

<sup>25</sup>K. A. Gschneider, Jr., in *Solid State Physics: Advances and Applications*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16, p. 275.