PHYSICAL REVIEW B VOLUME 26, NUMBER 7 1 OCTOBER 1982

Reversible step rearrangement and segregation on nickel surfaces at the Curie temperature

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(Received 8 March 1982)

Reversible step period rearrangement and carbon segregation have been observed on clean nickel single-crystal surfaces whose bulk is also relatively free of impurities. These transitions occurred over a temperature range of 35 K at the nickel Curie temperature, as determined by simultaneous low-energy electron diffraction, Auger, and permeability measurements on nickel stepped and flat (111) surfaces. The observation of segregated carbon in carbidic form (isolated carbon atoms) indicates an unusual bonding state of C to the surface below the Curie temperature. Measured carbon coverages indicate a change in the heat of segregation of greater than 0.2 eV per carbon atom at the Curie point.

I. INTRODUCTION

Experimental results published by several research groups within the last few years demonstrate changes in the chemical properties of magnetic surfaces at the Curie temperature T_C. These results indicate that changes in the surface electronic structure associated with the ferromagnetic-paramagnetic transition affect the activation energy of metals for a variety of chemical processes. In particular, the oxidation rates of iron and nickel and various alloy surfaces are described by different activation energies above and below the Curie temperature.[1-6] In iron, a change of 10 kcal/mole in the activation energy for oxidation has been reported[1,2]; for nickel, 24 kcal/mole is the reported change.[3]

The sublimation rate for cobalt metal has been studied in the vicinity of its Curie temperature.[7] For cobalt a change of 18 kcal/mole in the activation energy for sublimation was reported at T_C. The reaction rate for CO with nickel to form $Ni(CO)_4$ has been studied. For this reaction a change of about 5 kcal/mole in the activation energy at the Curie temperature was observed.[8]

In this paper we report low-energy electron diffraction (LEED) and Auger observations made on the nickel (111) surface and on stepped nickel surfaces with (111) terraces. Reversible step rearrangements have previously been reported for these stepped surfaces at temperatures in the range 350–400 °C.[9] We used LEED to monitor average step widths over this temperature range. By measuring simultaneously the ac permeability of the nickel crystals, we have observed that the step arrangements occur in the immediate vicinity of the Curie temperature. This is the first observation of a reversible surface morphological transformation associated with the bulk ferromagnetic-paramagnetic transition.

We have also used Auger electron spectroscopy to monitor the surface composition of both the stepped and flat Ni(111) surfaces. We have observed very small amounts of carbon ($\sim$0.2 monolayer) segregating reversibly in the vicinity of the Curie temperature on these surfaces, which are otherwise clean. We attribute the segregation to a change in the heat of segregation of greater than 4 kcal/mole. The Auger spectra indicate that the segregated carbon is bonded in a manner not previously reported on Ni(111) flat or stepped surfaces, suggesting that surface electronic states may change at the Curie point.

II. EXPERIMENTAL

We shall employ the convention introduced by Thapliyal to describe the orientation of stepped surfaces.[10] A surface described by $(111)\alpha^\circ[abc]$ indicates departure from the (111) plane by a rotation of angle α in the $[abc]$ zone of the stereographic triangle.

The LEED and Auger measurements were performed on the samples under ultrahigh vacuum conditions ($<5\times10^{-10}$ Torr pressure). Our samples were prepared from two single-crystal rods obtained from different sources. The crystals were cut into ribbons about 2-cm long and 0.6-cm wide and then polished. After polishing, the crystals were etched for strain relief. Ni(111) and Ni(111) 10°[$1\bar{1}0$] crystal surfaces were cut from one rod. Consequently, we assumed that these two samples had the same bulk carbon impurity levels. A Ni(111) 5°[$1\bar{1}0$] crystal surface was cut from the other rod. The crystal orientations were established within 0.5° using x-ray diffraction.

After mounting in the vacuum system, the crystal surfaces were cleaned by a combination of heating and argon-ion sputtering. Crystal cleaning for these experiments was complicated by the fact that the measurements were performed at temperatures allowing equilibration between bulk impurities and the surface. Preliminary Auger studies showed small amounts of carbon (<0.2 monolayer) at temperatures $<350\,^\circ$C and no detectable carbon (<0.003 monolayer) at higher temperatures. Small amounts of sulfur, phosphorus, and chlorine (<0.2 monolayer) were detected at higher temperatures. The sulfur, phosphorus, and chlorine were removed by several cycles of heating to 600 °C alternated with quenching and ion bombardment. After the cleaning, the surface showed less than 0.05 monolayer of any impurity at temperatures above 350 °C even after extensive annealing. As described in Sec. IV, approximately 0.1 monolayer of carbon appeared on the crystals after annealing at temperatures below 350 °C. Attempts to remove the bulk carbon by heating in 3×10^{-6} Torr oxygen at 600 °C produced highly oxidized surfaces which were not readily cleaned by ion bombardment. Consequently, experiments were performed for both step rearrangement and carbon segregation on nickel crystals which contained small amounts of carbon as a bulk impurity. We emphasize that surface impurities were less than 0.1 monolayer for the step rearrangement experiments. The carbon which appeared below 350 °C had a carbidic Auger peak shape. Graphitic Auger peaks were not observed at any temperature even after extensive annealing. We conclude that the bulk carbon precipitation temperature was well below 350 °C implying a very small ($\ll 10^{-3}$ at. %) carbon impurity level in these crystals.[11]

Figure 1 shows the experimental arrangement used. The crystals were spot welded to nickel support wires having the same cross-sectional area as the crystals in order to ensure uniform resistive

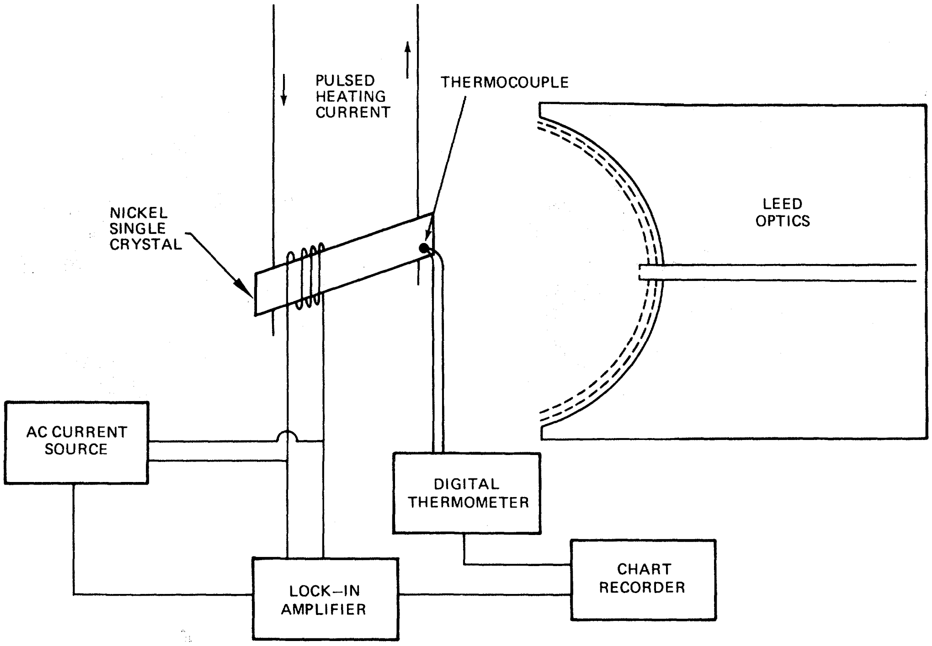

FIG. 1. Experimental arrangement to measure LEED pattern changes and permeability with temperature.

heating. The crystals were heated using a 50-Hz square-wave current with simultaneous gating of the LEED suppressor grid as described previously.[12] This ensured that the LEED spots were observed only when the heating current was off, thus avoiding any magnetic deflection of the diffracted beams. In order to monitor the bulk permeability during surface measurements a small coil was placed around half of the length of the crystal. A 20-kHz constant current source drove the coil and the resultant ac voltage across it was measured by phase-sensitive detection. The ferromagnetic-paramagnetic transition was easily detected by the large change in the voltage across the coil.

III. MORPHOLOGICAL STEP TRANSFORMATION OF NICKEL SURFACES IN THE VICINITY OF THE CURIE TEMPERATURE

Morphological phase transformations on stepped nickel surfaces in the $[1\bar{1}0]$ zone vicinal to the (111) surface have been studied previously by Thapliyal and Blakely.[9] They reported a change in the average step height and spacing at 360±10 °C for Ni(111) 10°$[1\bar{1}0]$ and at about 400 °C for Ni(111) 5°$[1\bar{1}0]$. For both these surface single atomic height steps were observed above the transition temperature. Below the transition temperature

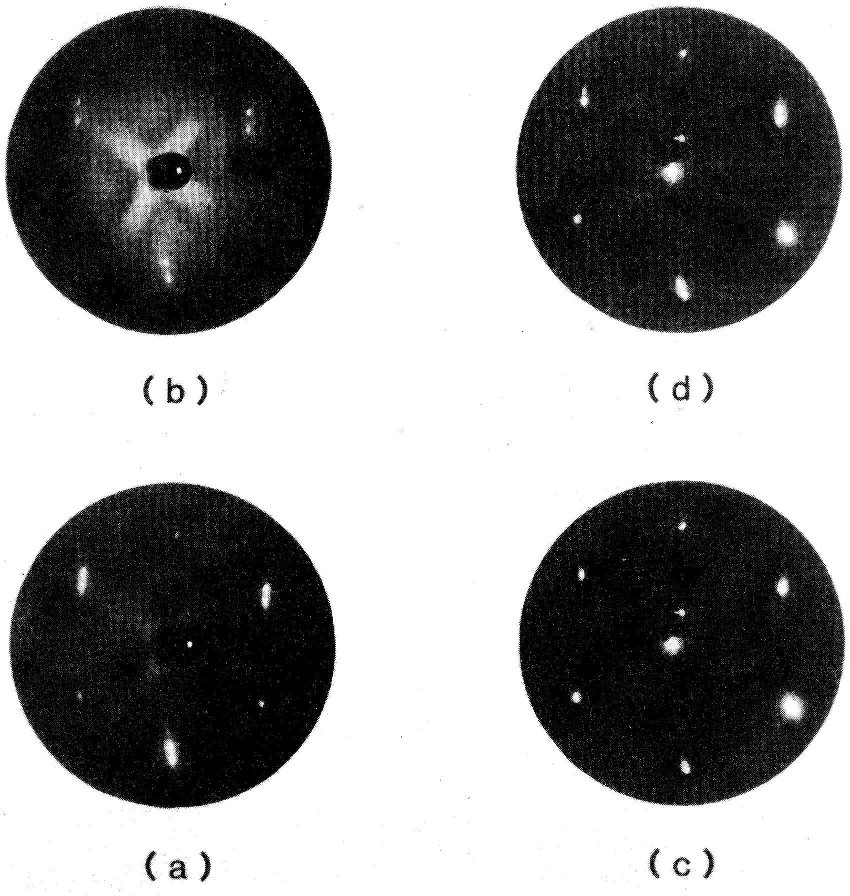

FIG. 2. LEED spot pattern from the Ni(111) 10°$[1\bar{1}0]$ surface, $E=157$ eV: (a) $T=100\,^\circ\mathrm{C}$, (b) $T=505\,^\circ\mathrm{C}$; LEED spot pattern from the Ni(111) 5°$[1\bar{1}0]$ surface: (c) $E=61$ eV, $T=330\,^\circ\mathrm{C}$, (d) $E=64$ eV, $T=440\,^\circ\mathrm{C}$.

the Ni(111) 5°$[1\bar{1}0]$ surface showed steps of four or five atomic heights. Below the transition temperature, the Ni(111) 10°$[1\bar{1}0]$ surface showed double atomic height steps.

The proximity of these morphological phase-transition temperatures to the Curie temperature (354 °C for pure nickel) suggests that there is some connection between the morphological transition and the paramagnetic-ferromagnetic transition. We have studied the step-rearrangement transitions for Ni(111) 10°$[1\bar{1}0]$ and Ni(111) 5°$[1\bar{1}0]$ surfaces using LEED with simultaneous monitoring of the bulk permeability as discussed in Sec. II. Figures 2(a) and 2(b) show LEED patterns taken using 157-eV electrons at normal incidence on the Ni(111) 10°$[1\bar{1}0]$ crystal held at 100 °C and 505 °C, respectively. The splitting of the spots in the LEED pattern corresponds to the reciprocal-lattice vector of the mean terrace periodicity for these stepped surfaces. For normal incidence, the average terrace spacing L is related to the angular separation of the split spots as follows[10]:

$$L=\frac{\lambda}{\Delta\phi_{hk}(\cos\phi_{hk}-\tan\alpha\sin\phi_{hk})}\,, \qquad (1)$$

where λ is the electron wavelength, ϕ_{hk} is the angle of the hk diffraction beam with respect to the 00 beam, α is the angle between the normal to the stepped surface and the normal to the nearest low-index plane, and $\Delta\phi_{hk}$ is the angular separation in radians between the split spots comprising the hk diffraction beam.

Using the electron energy and the spot splitting shown in Figs. 2(a) and 2(b), from Eq. (1) the mean repeat distance of the terraces on the Ni (111) 10°$[1\bar{1}0]$ surface is 14 Å at the high temperature and 20 Å at the low temperature. These distances are approximate since the errors caused by the window and the angle of observation could be as large as 2 Å. Mean step heights determined for the 10° crystal from the step length and angle α are 2.5 Å at high temperature and 3.6 Å at low temperature, again with $\pm 10\%$ accuracy. The bulk spacing of Ni(111) planes is 2.03 Å.

A spot photometer was used to determine the temperature range of the step-rearrangement transition. The field of the photometer was limited to approximately twice the diameter of one component of the split (01) beam. The field was centered on the upper spot of the split pair as shown in the inset of Fig. 3. The electron energy was 112 eV. As the temperature was increased the spot splitting changed upon passing through the step-rearrangement temperature. The field of the spot photometer was selected so that the observed component of the split (01) beam had relocated just outside of the photometer field after the step rearrangement. Thus the spot photometer measurement of the intensity collected at a fixed position on the LEED screen provided a sensitive monitor of the morphological phase transformation on the stepped surface. The crystal temperature was increased (or decreased) at a rate of approximately 0.2 °C/sec.

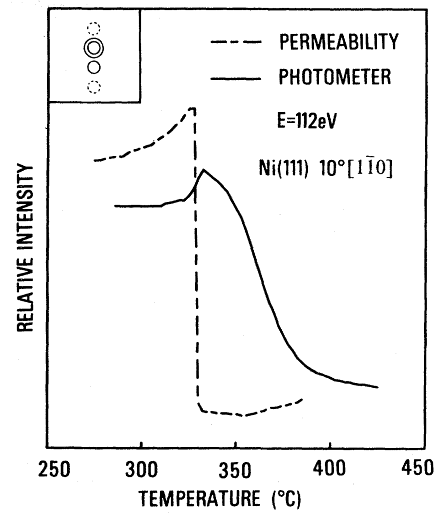

FIG. 3. Spot photometer intensity and relative permeability vs thermocouple temperature from the Ni(111) 10°$[1\bar{1}0]$ stepped surfaces at $E=112$ eV. The inset shows spot position of the split (01) beam with respect to photometer field for low-temperature (solid) and high-temperature (dotted) phases.

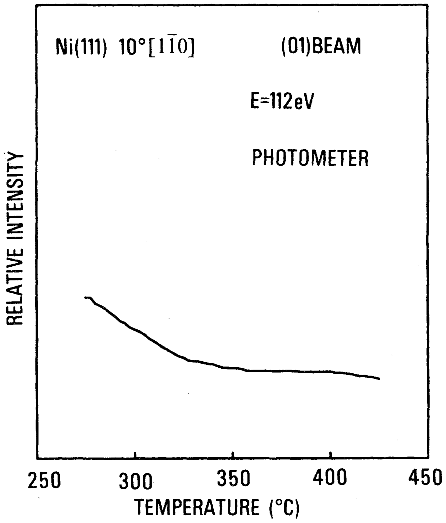

FIG. 4. Spot photometer intensity of (10) beam (unsplit) at $E=112$ eV vs thermocouple temperature.

This rate gave reproducible transitions which were free of hysteresis.

In Fig. 3 the intensity collected by the spot photometer and the ac voltage developed across the permeability monitoring coil are plotted as a function of thermocouple temperature. The change in the intensity collected by the spot photometer in the vicinity of 350 °C is attributed to the change of terrace spacing on the Ni(111) 10°[$1\bar{1}0$] surface. It is clear that the temperature range of the morphological transformation and the bulk Curie transition overlap. The step rearrangement occurs over a wider temperature range than the bulk Curie transition.

We also recorded the photometer intensity of one of the unsplit LEED spots at the same incident electron energy. Figure 4 shows the intensity in the spot photometer field centered on the unsplit (10) beam as a function of temperature. The relative intensity scale for the photometer is identical to that in Fig. 3. The Ni LEED intensities show a Debye-Waller dependence on temperature; however, no discontinuities are observed in intensities. Changes in position of all the LEED spots due to magnetic fields changing at the Curie temperature are thereby ruled out.

Similar LEED measurements were made on the stepped Ni(111) 5°[$1\bar{1}0$] surface. The LEED patterns are shown for $E=61$ eV, $T=330$ °C, and $E=64$ eV, $T=440$ °C in Fig. 2(c) and 2(d), respectively. Because of the greater terrace width, the split LEED spots are separated by a smaller angle than for the 10° crystal, making accurate terrace determination difficult. From the data of Fig. 2(c) and 2(d) we obtain a mean-terrace repeat distance of 24 Å at $T=440$ °C and > 80 Å at $T=330$ °C.

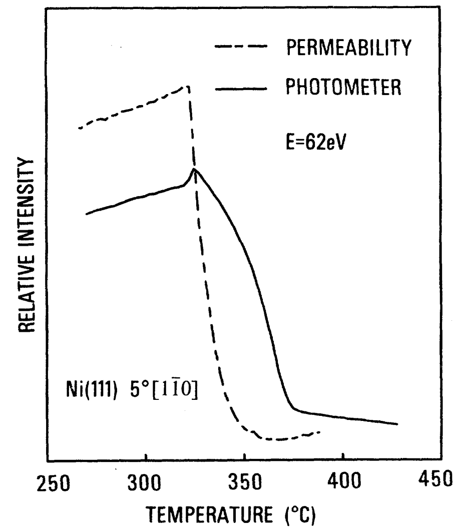

FIG. 5. Spot photometer intensity of a split (11) beam and permeability vs thermocouple temperature from the Ni(111) 5°[$1\bar{1}0$] stepped surface at $E=63$ eV.

Figure 5 shows the correlation between spot photometer and permeability data for the Ni(111) 5°[$1\bar{1}0$] surface. At $E=62$ eV, the spot photometer field was centered on one spot of the (11) beam in the manner already described. The step rearrangement again begins in the immediate vicinity of the Curie temperature.

The LEED patterns for both the 5° and 10° vicinal surfaces showed alignment of the stepped surfaces along the (110) crystal axis as expected. This differs from the results of Thapliyal and Blakely,[9] which shows steps on the 5° surface occuring at an angle to the (110) axis. The crystals prepared by Thapliyal and Blakely differed from those used here primarily in having a much higher concentration of carbon with a precipitation temperature above the Curie temperature.

IV. SEGREGATION OF CARBON TO NICKEL SURFACES IN THE VICINITY OF THE CURIE TEMPERATURE

Blakely and co-workers have studied carbon segregation to a variety of carbon-doped nickel single-crystal surfaces.[13–16] For the Ni(111), Ni(111) 5°[$1\bar{1}0$], and Ni(111) 10°[$1\bar{1}0$] surfaces, they report the segregation of a monolayer of graphitic carbon at a temperature $T_s=1.12T_p$.[13,16] Upon lowering the temperature to T_p, the bulk carbon precipitation temperature, they observed increased quantities of graphitic surface carbon. Above T_s, the surface was free of any detectable carbon.

Our segregation results for carbon on Ni(111), Ni(111) 5°[$1\bar{1}0$], and Ni(111) 10°[$1\bar{1}0$] are very different from those of Blakely *et al.*[13,16] Our crystals were prepared from Marz grade nickel which was subsequently zone-pass refined. One would expect a relatively low bulk carbon impurity level for crystals prepared in this manner. At high temperature no carbon was detectable using Auger spectroscopy on these crystal surfaces even after extensive annealing (24 h) at 600, 500, or 400 °C. Carbon observed below 350 °C would not be attributed to precipitation since the Auger peak shape was carbidic.

The experiment was identical to the arrangement shown in Fig. 1 except that the Ni crystal surface was rotated to a position in front of a coaxial electron gun and cylindrical mirror analyzer to do

Auger analysis of surface constituents. In addition to ordinary differentiated Auger spectra taken at fixed temperatures, it was possible to perform rapid analysis by multiplexing between specified elemental Auger lines as a function of thermocouple temperature. In this manner we are able to monitor the impurities associated with nickel: carbon, oxygen, sulfur, phosphorus, and chlorine.

By repeated cycles of heating at 500–600 °C, quenching, and argon sputter ion bombardment, we were able to obtain annealed stepped and flat Ni(111) surfaces which showed less than 0.01 monolayer (typically 0.005 monolayer) of the above impurites, even after prolonged heating. If, instead of quenching, the crystal temperature was slowly lowered through 350 °C, carbon was observed to segregate on the stepped and flat surfaces. Precipitation of carbon (as indicated by a graphitic Auger peak shape) was never observed. We conclude that the precipitation temperature for these crystals was less than about 300 °C. This corresponds to a carbon impurity level less than about 200 ppm based on extrapolation of published solubility data for carbon in nickel.[12]

In Figs. 6 and 7 the carbon coverage on the Ni(111) 5°[110] and Ni(111) 10°[110] surfaces is plotted as a function of temperature for both heating and cooling. The heating and cooling curve show only a small amount of hysteresis implying that near equilibrium conditions existed during these measurements. The carbidic Auger peak shape observed implies that the segregation is occurring to isolated sites on these surfaces. This major difference in segregation behavior from that observed by Blakely *et al.*[13,16] can be attributed to the much lower carbon doping level in our crystals which precludes precipitation in the vicinity of the Curie point. Figures 6 and 7 also show permeability data obtained on these crystals in this temperature range. The occurrence of segregation in the immediate vicinity of the Curie temperature suggests a relationship between the segregation of carbon on these surfaces and the ferromagnetic transition of nickel. As discussed in Sec. III, a step rearrangement occurs on these surfaces vicinal to (111) in this same temperature range.

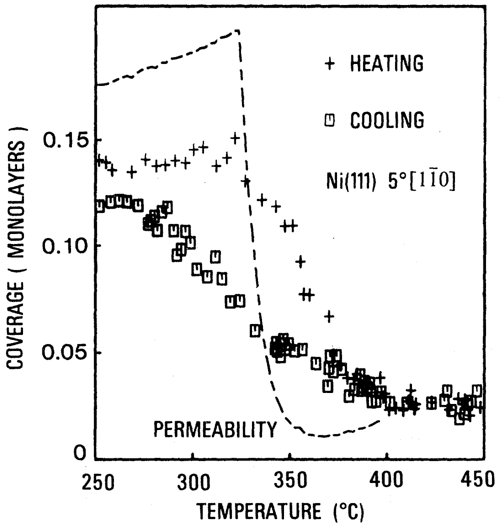

FIG. 6. Carbon coverage of the Ni(111) 5°[1$\bar{1}$0] stepped surface vs thermocouple temperature. The permeability is also shown as a dashed line.

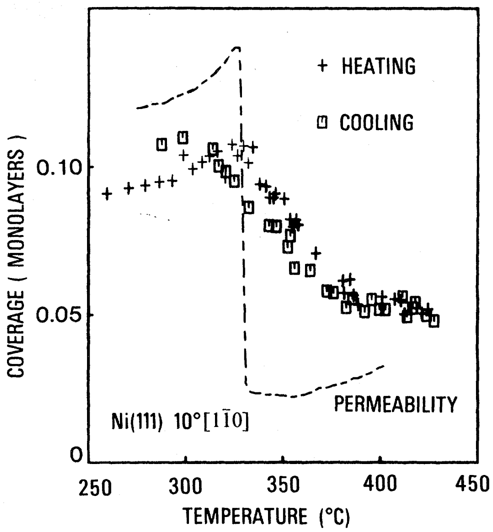

FIG. 7. Carbon coverage of the Ni(111) 10°[1$\bar{1}$0] stepped surface vs thermocouple temperature. The permeability is shown as a dashed line.

It is possible that the segregation on the stepped surfaces may be due to altered surface morphology above and below the step-rearrangement temperature. Alternatively, the step rearrangement might be drived by segregation of carbon which changes the surface free energy, particularly at corner sites.

In order to clarify the relationship between the surface carbon segregation, the step rearrangement, and the Curie temperature, the segregation experiements were also performed on flat Ni(111) surfaces. On the Ni(111) surface the kinetics of segregation were somewhat slower than on the stepped surfaces. Consequently, we measured the equilibrium surface carbon concentration at two temperatures, 356 and

316 °C. The corresponding Auger spectra are shown in Fig. 8. No carbon was detectable after 12 h at 356 °C. After 12 h at 316 °C, 0.3 monolayer of carbidic carbon was present. The carbon segregation was reversible since raising the temperature from 316 to 356 °C, casued the segregated carbon to disappear, presumably into bulk solution. These observations indicate that 0.3 monolayer of carbon segregated reversibly below the Curie temperature on Ni(111).

We have also observed the step-rearrangement transition on stepped surfaces at increased rates of heating and cooling. At a rate of up to 1 °C/sec, it was still possible to observed the step rearrangement reversibly. This rate was too rapid for equilibrium coverages of segregating carbon to reach the surface by diffusion.

The occurrence of segregation on the flat Ni(111) surface indicates that surface segregation occurs at the Curie point independent of step rearrangements. For stepped surfaces containing carbon, the rapid kinetics of the step rearrangement relative to the surface segregation suggest that the two phenomena may be independent.

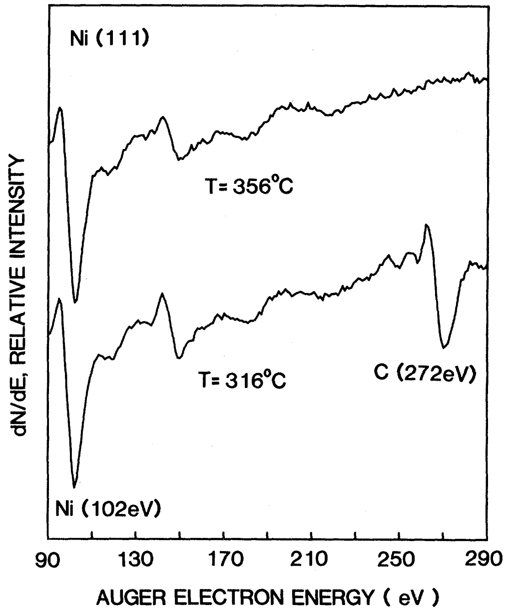

FIG. 8. Auger spectra of the Ni(111) surface taken above and below the Curie temperature, showing the reversible appearance of 0.3 monolayer of segregated carbon. The carbon appears with a carbide line shape.

V. DISCUSSION

Previous experiments by Blakely and co-workers show no segregation of carbidic carbon in Ni(111), Ni(111), 5°[1$\bar{1}$0], or Ni(111) 10°[1$\bar{1}$0].[13,16] We have observed the segregation of carbidic carbon on these surfaces, but only at temperatures below the Curie temperature T_C. The mechanism for segregation on nickel below T_C appears different from that for segregation at higher temperatures. We use a Langmuir model for segregation since the carbidic line shape shows that segregation occurs to isolated surface sites. The surface concentration of segregated solute atoms X_s is related to the bulk concentration X_b as follows:

$$\frac{X_s}{1-X_s}=\frac{X_b}{1-X_b}\exp\left[\frac{S}{k}\right]\exp\left[-\frac{H}{kT}\right], \tag{2}$$

where S is the entropy change due to segregation, and H is the heat of segregation.

One possibility is to assume that normal segregation following the Langmuir model is taking place in the vicinity of 350 °C. If we attempt to fit the data of Figs. 6 and 7 by this simple model, an unreasonably large heat of segregation of $+1.88$ eV/atom results. This is most unlikely since the experiments of Blakely *et al.*[13] show no segregation to isolated sites implying that the heat of segregation is negative for carbon on Ni(111).

We suggest on the basis of these results that the heat of segregation for carbon on these nickel surfaces changes at the Curie point.[17] If S and H are the entropy and heat of segregation above the Curie point, and S' and H' are the entropy and heat of segregation below the Curie point, we have

$$\frac{X_s'}{1-X_s'}=\frac{X_b}{1-X_b}\exp\left[\frac{S'}{k}\right]\exp\left[-\frac{H'}{kT}\right],\quad T<T_C \tag{3a}$$

$$\frac{X_s}{1-X_s}=\frac{X_b}{1-X_b}\exp\left[\frac{S}{k}\right]\exp\left[-\frac{H}{kT}\right],\quad T>T_C \tag{3b}$$

where X_s' is the surface carbon coverage below the Curie point and X_s is the surface carbon coverage above the Curie point. If we assume no change in the entropy of segregation at the Curie point ($S=S'$) and evaluate for coverages immediately above and immediately below the Curie point, we find

$$\frac{X_s(1-X_s')}{X_s'(1-X_s)}=\exp\left[\frac{H'-H}{kT_c}\right]. \tag{4}$$

From the Auger data on Ni(111) we estimate coverages above and below the surface coverage change of $X_s < 0.003$ monolayer and $X_s' = 0.23$ monolayer.

We conclude that $(H' - H) > 0.2$ eV/atom. The work of Blakely *et al.* implies that H is positive since no surface segregation to isolated surface sites was observed on Ni(111) or surfaces vicinal thereto. Our data implies that the heat of segregation for carbon on Ni(111) below the Curie point is negative and that the change in the heat of segregation at the Curie point must be greater than 0.2 eV.

ACKNOWLEDGMENTS

The authors would like to thank Dr. J. M. Blakely and Dr. L. M. Falicov for stimulating discussions. This work was supported in part by the Office of the Environment, and the Office of Basic Energy Sciences, Department of Energy.

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[1] J. C. Measor and K. K. Afzulpurker, Philos. Mag. 10, 817 (1964).

[2] B. C. Sales, A. L. Cabrera, and M. B. Maple, Solid State Commun. 30, 119 (1979).

[3] B. C. Sales and M. B. Maple, Phys. Rev. Lett. 39, 1636 (1977).

[4] H. H. Uhlig and A. S. Brasunas, Electrochem. Soc. J. 97, 448 (1950).

[5] H. H. Uhlig, Act Metall. 4, 541 (1956).

[6] H. H. Uhlig, J. Pickett, and J. Macnairn, Acta. Metall. 7, 111 (1959).

[7] B. C. Sales, J. E. Turner, and M. B. Maple. Phys. Rev. Lett. 44, 586 (1980).

[8] R. S. Mehta, M. S. Dresselhaus, G. Dresselhaus, and H. J. Zeiger, Phys. Rev. Lett. 43, 970 (1979).

[9] H. V. Thapliyal and J. M. Blakely, J. Vac. Sci. Technol. 15, 600 (1978).

[10] H. V. Thapliyal. Ph.D. thesis, Cornell University, 1977 (unpublished).

[11] J. J. Lander, H. E. Kern, and A. L. Beach, J. App. Phys. 23, 1305 (1952).

[12] J. C. Hamilton, J. Phys. E 11, 399 (1978).

[13] J. C. Shelton, H. R. Patil, and J. M. Blakely, Surf. Sci. 43, 493 (1974).

[14] L. C. Isett and J. M. Blakely, Surf. Sci. 47, 645 (1975).

[15] L. C. Isett and J. M. Blakely, Surf. Sci. 58, 397 (1976).

[16] M. Eizenberg and J. M. Blakely, J. Chem. Phys. 71, 3467 (1979).

[17] J. C. Hamilton and Terrence Jach, Phys. Rev. Lett. 46, 745 (1981).

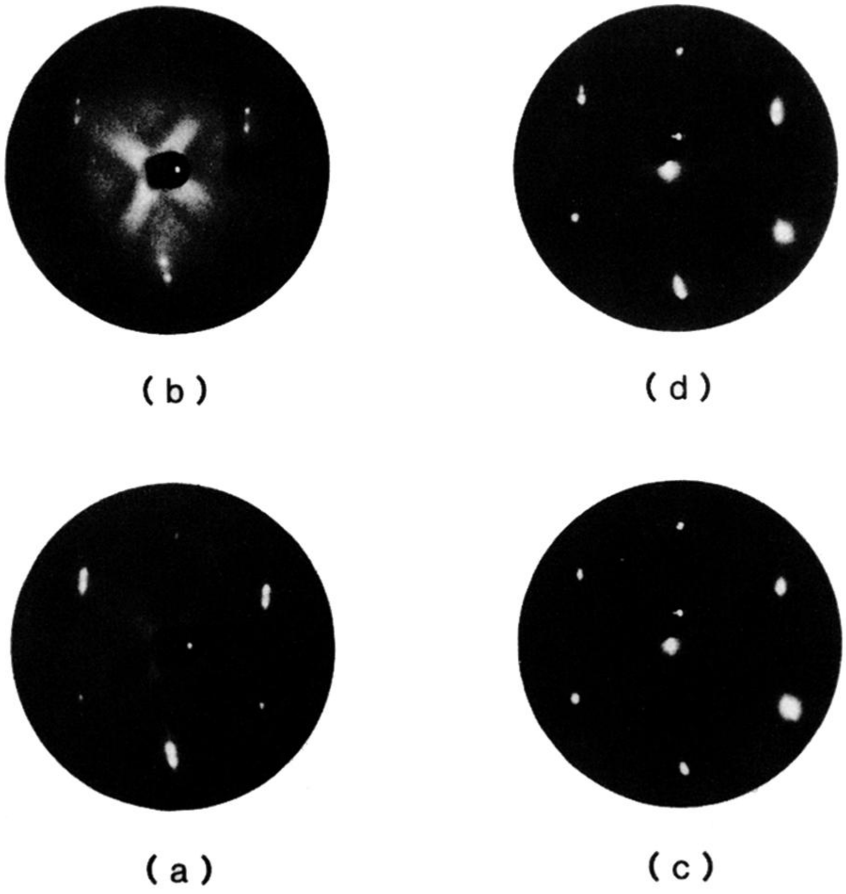

FIG. 2. LEED spot pattern from the Ni(111) 10°[$1\bar{1}0$] surface, $E=157$ eV: (a) $T=100\,^{\circ}\mathrm{C}$, (b) $T=505\,^{\circ}\mathrm{C}$; LEED spot pattern from the Ni(111) 5°[$1\bar{1}0$] surface: (c) $E=61$ eV, $T=330\,^{\circ}\mathrm{C}$, (d) $E=64$ eV, $T=440\,^{\circ}\mathrm{C}$.