$E_s \simeq 8$ °K and, therefore, $\Delta_0 \simeq 25$ °K. The available magnetic susceptibility data above 6 °K has, indeed, an activation energy of ~ 25 °K, while data at lower temperatures should confirm the soliton activation energy. The observed hysteresis at 1.5 °K is ~ 10% and implies strong coupling with $\eta \simeq 0.6$. The hysteresis should vanish when $T \simeq E_s$, and indeed it vanished above 5.5 °K.[17]

Note added.—I wish to thank Dr. S. A. Brazovskii for bringing to my attention, after the submission of this manuscript, his work on the fermion problem.[26] They consider only the fermion problem in the $\Lambda \to \infty$ limit; their result agrees with mine in this limit. I also wish to thank Professor J. R. Schrieffer and Dr. E. Domany for very useful discussions.

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Structural Phase Transitions in Nickel at the Curie Temperature

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It is observed that a reversible step period rearrangement on clean nickel single-crystal surfaces occurs in the immediate vicinity of the Curie temperature. Reversible carbon segregation is observed on the same crystal surfaces below the Curie point. The segregated carbon is carbidic, not graphitic, and indicates a change in the nickel surface electronic structure occurring at the ferromagnetic transition. Measured carbon coverages indicate a change greater than 0.2 eV per carbon atom in the heat of segregation at the Curie point.

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Several recent experiments have focused attention on changes in the chemical properties of magnetic surfaces at the Curie temperature.[1-5] These experiments indicate a direct connection between the magnetic state of the surface and the binding energy of adatoms on the surface. In this Letter we report strong evidence of a new and significant phenomenon, a reversible *structural* surface phase transition directly coupled to the ferromagnetic transition of nickel.

We have observed that a reversible change in morphology of several different stepped single-crystal surfaces occurs in the immediate vicinity of the Curie temperature. Using low-energy electron diffraction (LEED) in ultrahigh vacuum, we have monitored the reversible change in step height and spacing on surfaces vicinal to the nickel (111) face first reported by Thapliyal and Blakely.[6] We have directly correlated the temperature range of the step rearrangement (350° to 380 °C) with the Curie temperature of the nickel crystals by measuring the ac permeability of the sample with changing temperature while taking the LEED data.

Additionally, Auger analysis of the same very clean crystal surfaces shows a sudden increase in surface carbon concentration, changing from negligible amounts to 0.1 monolayer, as the crystal temperature is lowered through the Curie point. We have observed both the step transition and the carbon segregation reversibly on nickel crystals cut at 5° and 10° from the (111) surface. The step transition and carbon segregation are probably related since carbon has been shown to induce morphological changes on stepped surfaces[6] and carbon segregation at nickel surfaces is itself dependent on the orientation of the face.[7] These observations are believed to be associated with changes in the electronic structure of the nickel surface.

The reversible step rearrangement is observed on nickel single crystals whose terraces and steps consist of (111) faces {surfaces vicinal to the (111) face in the $[1\bar{1}0]$ zone}. Surfaces vicinal to the (111) face in the $[01\bar{1}]$ zone do not show a transition.[6] The steps on these surfaces describe an approximately periodic linear grating. The reciprocal lattice vector of this grating manifests itself in LEED as a splitting of spots in the normal 1×1 diffraction pattern from the Ni(111) surface under appropriate diffraction conditions. This measurement of spot splitting thus provides a direct determination of average spacing between steps. Above the Curie point single atomic height steps with narrow terraces are observed (broader splitting); at lower temperatures multiple atomic height steps with wider terraces are observed (narrower splitting).

Our samples consisted of two nickel single crystals obtained from separate sources, cut and polished to give $(111)\times5°[1\bar{1}0]$ and $(111)\times10°[1\bar{1}0]$ surfaces.[8] The crystals were each cut into ribbon form approximately 2 cm long and 0.6 cm wide. The crystals were mounted on a manipulator which permitted resistive heating by a current through the longitudinal axis of the crystal, and temperature monitoring with a Chromel-Alumel thermocouple spot welded to one edge of the crystal. A small coil surrounded half the length of the ribbon crystal, allowing permeability measurements during Auger or LEED studies. A 20-kHz constant-current source drove the coil and the resultant ac voltage across it was measured by phase-sensitive detection.

Each crystal was initially cleaned by argon sputter-ion bombardment. This was followed by several cycles of heating in the vicinity of 600 °C for 15 min alternated with quenching and ion bombardment. After two to three cycles of cleaning followed by extensive annealing at 500 °C, the surface showed less than $\frac{1}{20}$ of a monolayer of any impurity.

Auger analysis of surface elements was performed with use of a cylindrical mirror analyzer and a 5-keV incident electron beam. The specific Auger lines monitored during the experiment were Ni (107 eV), S (150 eV), Cl (180 eV), C (271 eV), and O (503 eV). The peak heights were recorded in rapid sequence with a multiplexer. All measurements were made in ultrahigh vacuum (3×10^{-10} Torr).

The LEED measurements were made with use of the fluorescent screen of conventional four-grid optics. The basic procedure was to select an electron momentum at which spots in the diffraction pattern were observed to split into pairs. One spot of a pair was observed in the defined field of a spot photometer and the photointensity was recorded as the temperature of the nickel crystal was varied. On passing through the transition temperature, the spot splitting changed and the spot left the defined photometer field. Abrupt changes in collected intensity thus indicated the step rearrangement as confirmed by visual observation. Each spot of a split pair was checked for identical mirror symmetry and repeatable behavior above and below the Curie temperature. Similar behavior was observed for both (00) and (01) LEED beams and at various electron energies for which splitting occurred. In order to rule out magnetostrictive changes in crystal position or crystal magnetic fields which could cause deflection of the LEED spots as the nickel crystal was heated or cooled through the Curie temperature, nonsplit spots were observed while sweeping the crystal from 200° to 500 °C. No abrupt shifts of spot intensity or position were noted. Spot intensities gradually decreased with

increasing temperature as described by the Debye-Waller factor.

The crystal samples were heated between 250 and 500 °C for the measurements, at a rate of 10 °C/min. Slower rates gave identical results and we are confident that near-equilibrium conditions were sustained over this temperature range. The very small amount of hysteresis observed between heating and cooling substantiates this conclusion. The heating current consisted of 60-Hz pulsed dc current with peak values of 10 A. The modulation frequency was selected to reduce effects on the thermocouple, permeability, and Auger signals to a negligible level. A retarding-grid blanking scheme used to observe the LEED pattern during the half cycle when the heating current was off has been described previously.[9]

Figure 1 shows the results of LEED, permeability, and Auger measurements on the Ni(111) $\times 5°[1\bar{1}0]$ crystal as a function of sample temperature. The finite width of the bulk permeability measurement is due to temperature variation over the entire sample volume. The LEED trace consists of the intensity collected ($E = 62$ eV) within a spot photometer field which contained one of the split (01) LEED spots at low temperature. The spot had relocated completely just outside of the field by the upper limit of temperature shown. The permeability and LEED results are essentially the same for increasing and decreasing temperature.

Figure 1(b) shows coverages determined by the peak-to-peak height of the carbon (271 eV) Auger peak over the same temperature range. Results are shown for measurements starting at both high and low temperatures to indicate that near equilibrium was achieved.

Figure 2 shows results for the Ni(111) $\times 10°[1\bar{1}0]$ crystal, which are substantially the same as those for the 5° vicinal surface.

The data for the two different crystals show that both the step rearrangement and the surface carbon segregation are directly correlated with the ferromagnetic transition. The widths of both phenomena are almost identical and begin in the immediate vicinity of the Curie point measured in the bulk.

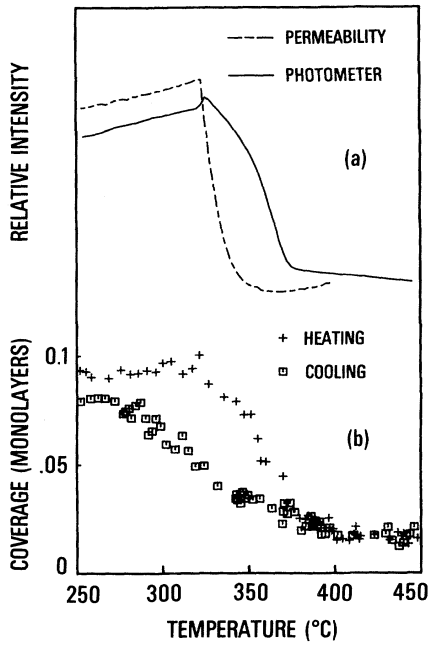

FIG. 1. Spot photometer, permeability, and carbon Auger intensities vs temperature for nickel single-crystal surface (111) $\times 5°[1\bar{1}0]$. (a) Solid line shows fraction of one LEED (01) spot within photometer field vs thermocouple temperature. The spot photometer field was fixed at low temperature on one of the pair of (01) beam spots split at $E = 62$ eV. Dashed line shows ac permeability of crystal vs temperature taken simultaneously with the photometer data. (b) Carbon coverage of surface by Auger intensity of C (271 eV) line vs thermocouple temperature. Heating and cooling curves taken at rates slower than 10 °C/min.

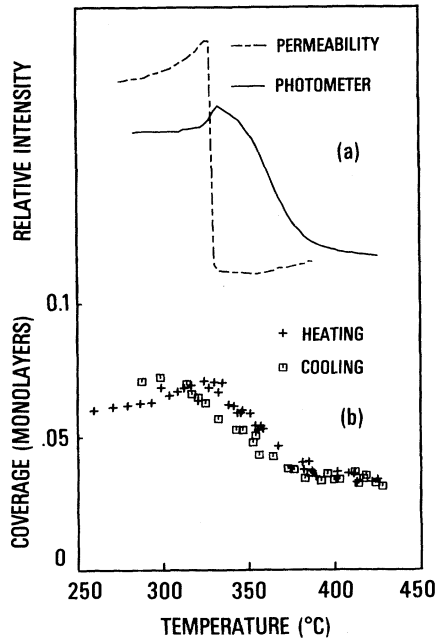

FIG. 2. Spot photometer, permeability, and carbon Auger intensities vs temperature for nickel single-crystal surface (111) $\times 10°[1\bar{1}0]$, plotted in the same manner as in Fig. 1.

It could be argued that the concentration of carbon dissolved in the bulk of each nickel crystal is such that we are observing carbon precipitation over a temperature range which fortuitously coincides with the Curie temperature. In that case, Auger spectra of the surface should show rapid growth of a large carbon peak with the graphite line shape previously reported for segregation and precipitation on the nickel (111) surface and surfaces vicinal to Ni(111).[10] However, Auger spectra taken on the crystal surfaces immediately after lowering to a temperature slightly below the Curie point show the growth of a carbon Auger peak of carbidic line shape (carbon-nickel bonds only), indicating the onset of segregation of a novel type at the Curie temperature in nickel. Furthermore, measurements made on flat, clean nickel (111) crystal surfaces indicated similar reversible carbon segregation in the vicinity of the Curie temperature, again with carbidic line shape. Carbon coverage observed was 0.2 monolayer just below the Curie temperature and undetected (< 0.003 monolayer) just above the Curie temperature. The kinetics of the segregation in the case of the flat (111) surface were very slow; details will be discussed in a subsequent paper.

The noninteraction of carbon atoms on the surface indicated by carbidic Auger spectra allows us to use the Langmuir model[11] to estimate magnetically related changes in the heat of segregation from surface carbon coverages measured above and below the Curie point. In this model the surface concentration of segregated solute atoms x_s is related to the bulk concentration x_b as follows:

$$\frac{x_s}{1-x_s} = \frac{x_b}{1-x_b} \exp\left(\frac{\Delta S}{k}\right) \exp\left(\frac{-H}{kT}\right),$$

where ΔS is the entropy change due to segregation and H is the heat of segregation. Using the coverage values given for the flat Ni(111) surface, and assuming that the entropy of segregation does not change on the flat surface at the Curie point, a change in the heat of segregation of at least 0.2 eV per carbon atom at the Curie temperature would result in the segregation coverage observed. This value is comparable with changes in the heats of sublimation inferred from previously reported experiments.[2-4]

The carbidic line shape (carbon-nickel bonds only) and low concentration of surface carbon lead us to conclude that we are observing segregation of a type not previously reported which results from a change in nickel surface states below the Curie temperature. The step rearrangement occurring over the same temperature range may be due to the change in surface free energy caused by the carbon segregation or direct nickel surface electronic structure changes at the Curie point or both together.

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