Initial oxidation kinetics near the Curie temperature of nickel

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The oxidation rate of nickel has been measured in the vicinity of its Curie temperature $\Theta_C = 631$ K in flowing oxygen at a pressure of one atomsphere by means of a gravimetric technique. The average oxide thickness x versus time t isotherms at each temperature T could be described by a simple power law: $\dot{x}(t) = A(T)t^{\alpha(T)}$. The dependence of the factor $A(T)$ on T is of the form $A(T) = A_0 \exp(-\Delta/T)$ with $A_0 = 2.1 \times 10^5$ Å and $\Delta = 5.1 \times 10^3$ K and apparently reflects an activated process, while the exponent $\alpha(T)$ increases monotonically with temperature from 0.17 at 570 K to 0.44 at 700 K. Oxidation rates were determined by differentiating the x vs t isotherms at a fixed oxide thickness x_0. For $x_0 \simeq 115$ Å, the oxidation rate follows two Arrhenius laws. For temperatures greater than Θ_C, the bulk Curie temperature of nickel, the activation energy is 36.8 ± 1 kcal/mole, while for temperatures smaller than Θ_C the activation energy is 61 ± 1 kcal/mole. In addition to the break in slope at Θ_C, there appears to be a small cusp-like feature near Θ_C. The observed modifications of the nickel oxidation kinetics are qualitatively consistent with recent theoretical predictions by Suhl.

I. INTRODUCTION

We have studied the oxidation of nickel in the vicinity of its Curie temperature ($\Theta_C = 631$ K) by means of a gravimetric technique. The purpose of the experiment was to determine the effect of the ferromagnetic-paramagnetic phase transition of nickel on its oxidation kinetics. The results reported here reveal a large difference in the oxidation kinetics, manifested as a change in activation energy of ~1 eV/atom between the paramagnetic and ferromagnetic phases of nickel. A preliminary account of these results has previously been given elsewhere.[1]

This experiment is part of a continuing investigation of the effects of bulk phase transitions on chemical reactions occurring at a substrate surface. Although only sparsely documented in the literature, this general class of phenomena is often referred to as the Hedvall effect.[2] If the connection between surface reaction rates and substrate phase transitions can be sufficiently well understood, it may then be possible to modify chemical-reaction rates at will by altering the electronic state of the substrate. Obviously, this is potentially very useful when the substrate is employed as a catalyst. For example, both the magnitude and direction of the magnetization of ferromagnetic nickel can be varied by applying external magnetic fields.

The oxidation of nickel was selected for initial investigation for a variety of reasons: (i) Oxidation is an important and relatively simple reaction which tends to dominate other gas-phase reactions with nickel. (ii) The growth of NiO is primarily by cation (nickel ion) migration.[3] This type of oxide growth is not sensitive to the oxygen pressure, but is sensitive to properties associated with the metallic surface, such as crystallographic orientation. Hence, for this type of oxide growth, the ferromagnetic phase transition should affect more strongly the oxidation kinetics. (iii) The rate of nickel oxidation is readily measurable in the vicinity of the Curie temperature using a gravimetric technique. The reaction is fast enough to measure, but slow enough to permit the study of thin NiO layers (~100 Å). (iv) Only one oxide is formed NiO and the oxide can be removed by hydrogen reduction so that the same Ni sample can be studied at all temperatures.[4] (v) The O_2 molecule possesses a magnetic moment which may couple to the magnetization of the Ni substrate (although for the data presented here, care was taken to insure that the net *macroscopic* magnetization was zero below the Curie temperature). (vi) Anomalies in chemical reaction rates near second-order phase transitions were recently predicted by Suhl[5] on theoretical grounds.

II. EXPERIMENTAL DETAILS

The nickel powder used was obtained by reducing small particles (60–125 μm) of NiO (Atomergic 99.999% pure) in flowing dry hydrogen at 673 K. The resulting powder was then sintered at 773 K for 90 h. As can be seen from Fig. 1, the surface area will continue to change even at temperatures below Θ_C if the powder is not presintered. Therefore, the ideal situation would be to presinter the nickel powder such that the surface area remains high but constant during the course of the experiment. For the nickel oxidation data presented here, the sample used weighed 85 mg and had a surface area of 75 ± 2 cm^2. The surface area of the
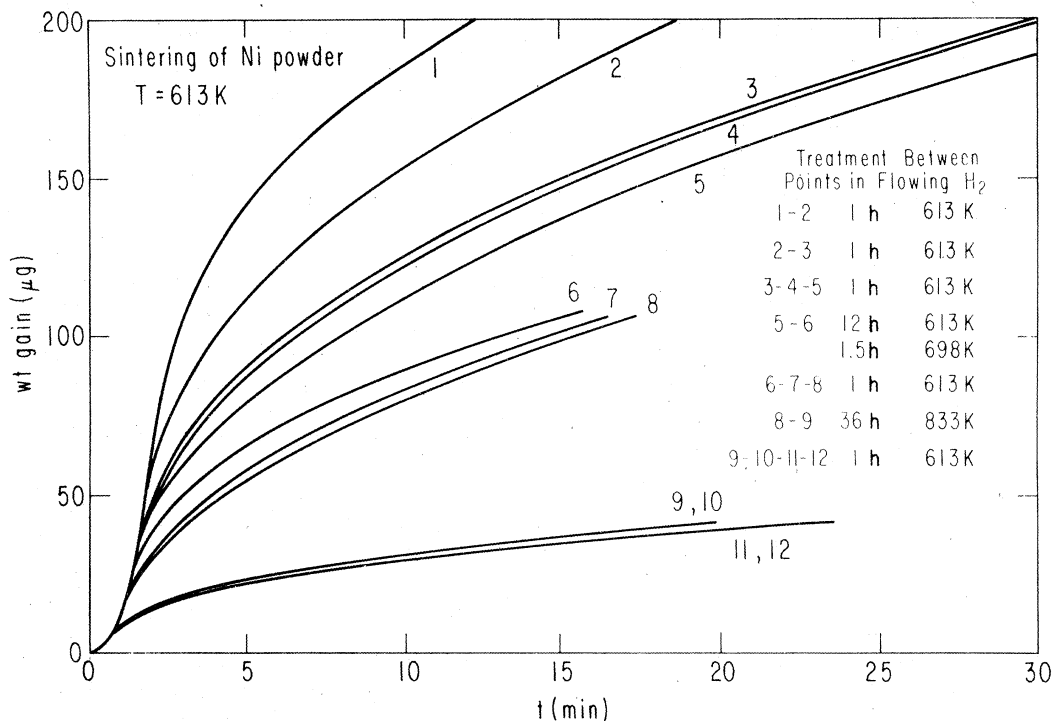
FIG. 1. Weight gain vs time isotherms for Ni oxidation at 613 K after repeated subjection of a 15.7-mg powdered Ni sample to flowing hydrogen at various temperatures between 613 and 833 K for various lengths of timing ranging from 1 to 36 h. Sintering of the sample is apparently complete after treatment at 833 K for 36 h in flowing hydrogen.

presintered nickel powder was determined by comparing the oxidation isotherms of the powdered sample with those obtained from a 0.025-mm-thick nickel foil with a geometric surface area of 16.8 cm^2 (assuming a surface roughness of 1 for the foil). A nickel foil was not used in these experiments for two reasons. First, in order to study the initial oxidation rates for oxide thicknesses less than 100 A, a foil did not provide a large enough ratio of surface area to weight. Second, the domain structure of a well annealed Ni foil below Θ_C changes with thermal cycling and it was felt that this may influence the oxidation rate. Such an effect would tend to be averaged out in a powdered sample where one has many domains with random orientations (all measurements were taken in zero magnetic field).

The nickel powder was placed in a hemispherical quartz cup with a diameter of 5 mm which was suspended with 0.005-in.-diam Pt wire from a Cahn RG microbalance which is capable of detecting weight changes of ±0.2 μg (see Fig. 2 for a schematic diagram of the apparatus).

Before each isotherm was taken, the nickel powder was reduced in flowing H$_2$ at 563 K for 15 min. It was found that reducing the sample at higher temperatures for longer times produced no sig-

nificant change in the subsequent oxidation isotherms and only increased the likelihood of unwanted sintering. The sample chamber was then flushed with N$_2$ gas and briefly evacuated to a pressure of about 10 mTorr. The chamber was again filled to 1 atm with N$_2$ gas which was then flowed over the sample at a rate of 30 cm^3/min. The temperature was raised to the temperature at which the oxidation isotherm was to be taken; after waiting for the balance and temperature to stabilize, the nitrogen valve was closed and the oxygen valve was opened. The oxygen flow rate was preset to a value of 30 cm^3/min. The oxidation isotherm was recorded with an automatic data acquisition system. When the isotherms were taken in this fashion, the reproducibility was within ±2%.

The temperature was monitored with a Chromel-Alumel thermocouple placed directly below the sample and stabilized to better than ±0.5 K with a simple feedback circuit. The actual temperature of the nickel was determined by measuring the bulk ferromagnetic transition temperature *in situ* by placing a small bar magnet outside the oven which produced a sufficient magnetic field and magnetic field gradient to give an apparent weight change of about 20 μg as the nickel was slowly
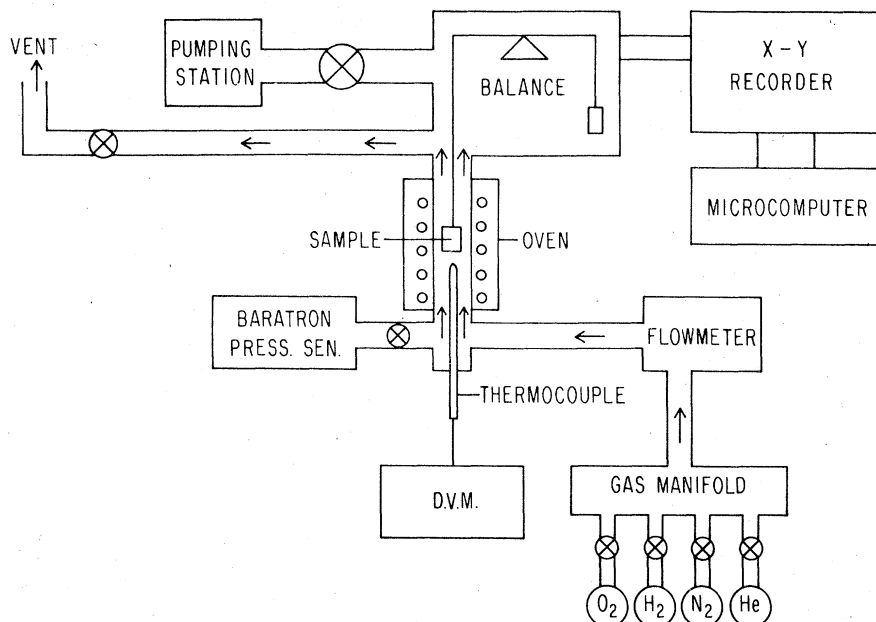
FIG. 2. Schematic dia-
gram of the apparatus used
to measure Ni oxidation
isotherms.

warmed or cooled through Θ_C. The temperature
of the thermocouple, which was typically about 10
K lower than the temperature of the nickel, was
corrected using the Ni Curie temperature as a cal-
ibration point.

The change from flowing N_2 to flowing O_2 gas is
accompanied by a change in both buoyancy and vis-
cosity which appears as an apparent change in
weight. This was measured by heavily oxidizing
the nickel at a relatively high temperature (450 °C),
and then measuring the buoyancy and viscosity cor-
rection at a lower temperature (275 °C). This cor-
rection amounted to between 1% and 10% of the to-
tal oxidation signal, and was found to be indepen-
dent of temperature over the temperature range
of interest.

III. RESULTS

Several typical Ni oxidation isotherms taken at
various temperatures between 587 and 648 K are
shown in Fig. 3. The solid line shown for each
isotherm was drawn through 120 data points taken
at 15-sec intervals, and the width of the line is
representative of the scatter in the data. We at-
tempted to fit the isotherms to various analytic
expressions derived in the literature, but found
that the best overall description of the data was
given by a simple power law

$$x = At^{\alpha}, \tag{1}$$

where x is the average oxide thickness in ang-
stroms, t is the time in minutes, and both A and
α depend on temperature. For t between 1 and 30

min, each isotherm was fitted by the method of
least squares to a line of the form

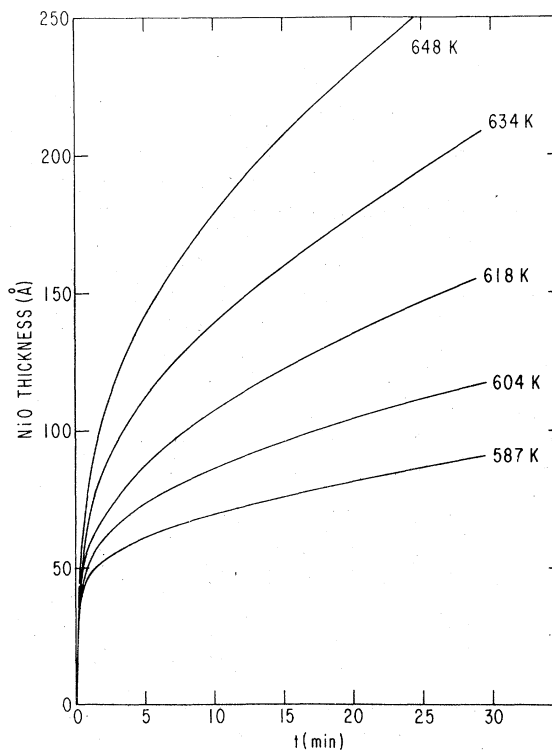$$\log x = \log A + \alpha \log t. \tag{2}$$

FIG. 3. Typical thickness x vs time t isotherms for
Ni oxidation for $t \leq 30$ min at various temperature be-
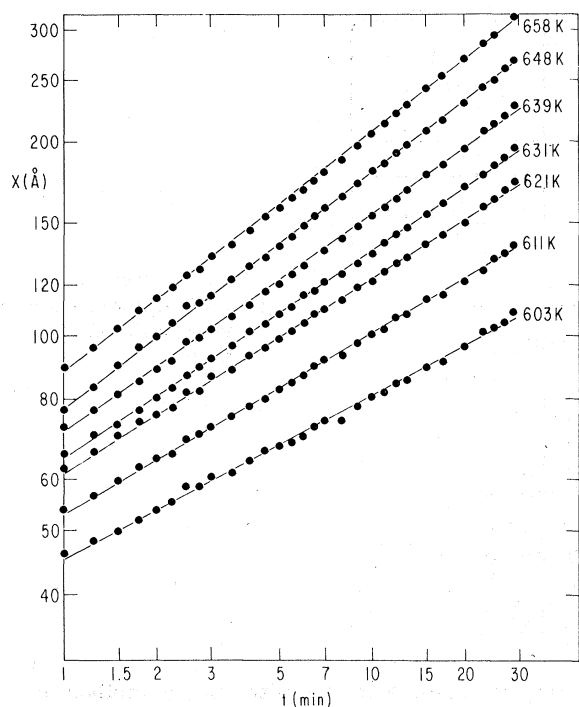tween 587 and 648 K (weight of Ni sample: 85 mg).

FIG. 4. Typical logarithm of thickness x vs logarithm of time t plots for Ni oxidation for $1 \leq t \leq 30$ min at various temperatures between 603 and 658 K (weight of Ni sample: 85 mg).

FIG. 5. (a) Factor A vs inverse absolute temperature. The solid line represents the function $A(T) = A_0 \exp(-\Delta/T)$, where $A = 2.1 \times 10^5$ Å and $\Delta = 5.1 \times 10^3$ K. (b) Exponent α vs absolute temperature. The solid line represents the function $\alpha(T) = \frac{1}{2}[1 - (T_0/T)^9]$, where $T_0 = 555$ K.

Several representative isotherms plotted as $\log x$ vs $\log t$ are displayed in Fig. 4. For most of the isotherms taken, the statistical correlation coefficient R was better than 0.999, while the absolute accuracy (reproducibility) of A and α was about $\pm 5\%$.

The temperature dependence of A and α are shown in Fig. 5. The parameter $A(T)$ appears to represent an activated process and can be described by

$$A(T) = A_0 \exp(-\Delta/T), \qquad (3)$$

where $A_0 = 2.1 \times 10^5$ Å and $\Delta = 5.1 \times 10^3$ K. The exponent α increases monotonically with temperature from 0.17 at 570 K to 0.44 at 700 K and can be described well by the function

$$\alpha(T) = \frac{1}{2}[1 - (T_0/T)^9], \qquad (4)$$

where $T_0 = 555$ K, although we are unable to attach any physical significance to the form of Eq. (4) at this time. Presumably, α cannot exceed the diffusion value of $\frac{1}{2}$ at high temperature, but unfortunately, it was not possible to determine α at temperatures much greater than 673 K due to problems associated with sintering.

Originally, we hoped to be able to study the rate of formation of the first one or two monolayers of
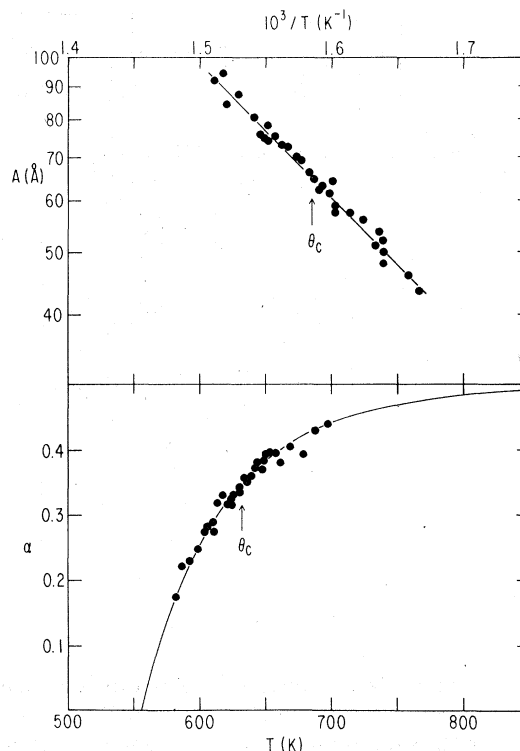
NiO, since in this thickness regime the physical properties of the nickel should have the largest effect on the oxidation rate. However, we found that the initial rate was limited not by surface kinetics, but rather by the rate at which oxygen could be delivered to the sample; i.e., at a given temperature, the initial oxidation rate was found to be roughly proportional to the oxygen flow rate. In addition, the initial few monolayers of NiO appear to be formed via an unactivated process, a result consistent with earlier work.[3] From room temperature to 500 K, the oxidation isotherms are essentially step functions with the initial "jump" in average oxide thickness Δx changing from about four monolayers at room temperature to eight monolayers at 225°C. If these data are expressed in the form of an Eyring plot $\lfloor \ln(\Delta x/T)$ vs $1/T\rfloor$, they yield an activation energy of 0.4 ± 0.2 kcal/mole, so that the initial oxidation is essentially unactivated. A possible mechanism for this unactivated initial oxidation has recently been advanced by Fehlner and Mott.[3]

Because of the very fast initial oxidation regime, the smallest oxide thickness at which we could ac-

curately determine the rate of NiO growth was about 100 Å. The rate r of Ni oxidation is defined as the rate of oxide growth at a fixed oxide thickness x_0. The oxidation rate was obtained from the data by least-squares-fitting each isotherm to Eq. (2) to determine A and α, and then differentiating Eq. (1); i.e.,

$$r \equiv \frac{dx}{dt}\bigg|_{x=x_0} = A\alpha t^{\alpha-1}\bigg|_{x=x_0} = A\alpha\left(\frac{x_0}{A}\right)^{(\alpha-1)/\alpha}, \qquad (5)$$

where $x_0 \cong 100$ Å. Figure 6 shows the rate of oxidation at an average oxide thickness of 115 Å plotted versus inverse absolute temperature in the vicinity of the Curie temperature of bulk nickel. At a temperature of 631 ± 2 K, there is a definite change in slope; for temperatures below 631 K, the activation energy is 61 ± 1 kcal/mole, whereas above 631 K, the activation energy is 36.8 ± 1 kcal/mole. The change in activation energy amounts to about 24 kcal/mole or 1 ev/atom. There also appears to be a small cusplike feature at 631 K. Although the experimental uncertainty is not much smaller than this feature, it was present in three separate measurements and is believed to be a real effect. Within an experimental uncertainty of ± 2 K, the break in slope shown in Fig. 6 occurs
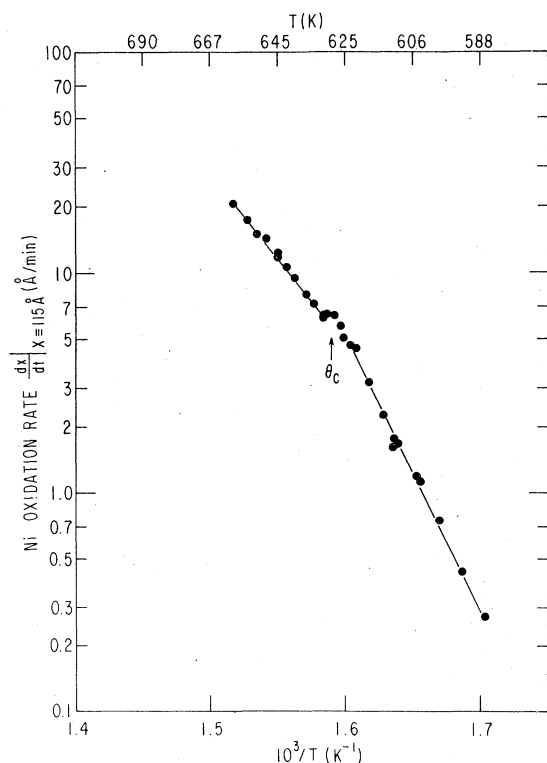

FIG. 6. Logarithm of the Ni oxidation rate dx/dt at $x = 115$ Å vs inverse absolute temperature.

exactly at the ferromagnetic transition temperature of *bulk* nickel. It was also found that the oxidation rate was more reproducible than either A or α and hence, within the resolution of the present experiment, it was not possible to determine whether primarily A or α changed at Θ_C.

The experiment was repeated on two different samples under slightly different conditions and virtually the same results were obtained. For one set of measurements, the oxygen flow rate was lowered to 8 cm³/min, while for another the sample was reduced in hydrogen at 673 K for 1 h between each isotherm.

IV. DISCUSSION

There have been many previous studies of the interaction of a nickel substrate with oxygen gas. However, most of the earlier work was restricted, to relatively high temperatures ~700–1000 K and thick NiO layers ~2000 Å,[6-8] or to low temperatures ~300 K and the first few monolayers of NiO.[9,10] Thus, it is difficult to compare these earlier results with those presented here. The low-temperature studies cited above indicate that at an oxide thickness of less than two monolayers, the surface layer is already characteristic of bulk NiO. At temperatures above 473 K, NiO crystallizes in a cubic NaCl structure.[4] Oxides of this type have no large channels through which the oxygen ions can diffuse, but do have interstitial and cation vacancies through which the smaller metal ions can migrate. Hence, for nickel oxidation, the growth is believed to be primarily by cation motion.[3]

If the oxide grows via cation migration, the nickel ion must first migrate from the metal surface to a vacancy in the oxide. To do this, the nickel atom must first overcome a potential energy barrier of height W, which is related to the energy necessary to break Ni-Ni bonds at the surface. In general, W can be considered to be the energy required to transfer a nickel atom through the metal-oxide interface. Once in the oxide, there will be another potential-energy barrier U for diffusion from one interstitial site to the next, but is generally believed that U is less than W.[11] Therefore, for thin oxide layers (~10–200 Å), the oxide growth rate will be limited by the time necessary for the surface Ni atom to overcome the first potential energy barrier W. If there are no other forces present, then the *initial* rate will be approximately given by

$$r \equiv \frac{dx}{dt} = BN\nu\exp\left(\frac{-W}{k_BT}\right), \qquad (6)$$

where B is a constant, N is the number of mobile Ni atoms at the surface, ν is the attempt frequency

(which will be the order of a phonon frequency), and the Boltzmann factor gives the probability that the nickel atom will succeed in escaping through the metal-oxide interface at temperature T.

If one includes the possibility of electric fields developing during the oxidation process, then the above rate will be modified. This was suggested by Cabrera and Mott,[11] who proposed that the oxygen ions which chemically adsorb at the oxygen-oxide interface provide traps for electrons with an energy eV below the Fermi level of the metal. It is assumed, at least in the thin film regime (~100 Å), that electrons from the metal can move rapidly through the oxide and fill these traps, which sets up an electrostatic potential V across the oxide. The electric field V/x then aids in pulling the Ni ions through the oxide. A similar effect can occur if the charge densities of electrons and metal ions are not equal within a region of the oxide. This can create a so-called "space-charge potential" which can effect the oxidation kinetics. If electric field effects are included, then the growth rate for thin oxide layers is approximately given by

$$ r \equiv \frac{dx}{dt} = BN\nu \exp\left(\frac{-W + eaV'(x)/x}{k_B T}\right), \qquad (7) $$

where e is the electronic charge, a is the order of the NiO lattice constant (4 Å), and $V'(x)$ takes into account both space charge effects and the potential V. The actual shape of the isotherms is obtained by integrating Eq. (7); however, this can be quite complicated since $V'(x)$ must be determined in a self-consistent fashion and specific assumptions must be made about cation, anion, and electron motion. In this paper, we make no attempt to determine V' but refer the interested reader to the work of Fromhold and co-workers who have investigated this problem in great detail.[12-14]

The experimental data shown in Fig. 6 indicate that the activation energy for temperatures below Θ_C is about 1 eV higher than the value for temper-

atures above Θ_C. It is difficult to envisage how a magnetic transition in the substrate could effect the electrostatic potential $V'(x)$ shown in Eq. (7). However, the energy necessary to remove a nickel atom from the surface W could be affected by the paramagnetic-ferromagnetic transition since in the ferromagnetic state, the nickel atoms are presumably more strongly bonded to the surface by an energy of the order of the exchange energy. The exchange energy, which is believed to be responsible for the ferromagnetism of nickel, has been estimated by Herring[15] to be of the order of 0.4 eV in the bulk.

It is noteworthy that both the cusplike feature and the change in activation energy near Θ_C observed in the experimental data displayed in Fig. 6 are qualitatively consistent with recent theoretical predictions by Suhl.[5] In Suhl's theory, the cusplike feature is attributed to changes in the prefactor of the reaction rate constant which arise from fluctuations in the substrate magnetization, whereas the change in activation energy is ascribed to the difference in Helmholtz free energy between the ferromagnetic and paramagnetic states of the substrate which results from the exchange field. Additional bonding due to the exchange energy is perhaps the simplest explanation for the change in the activation energy of the oxidation rate at the Curie temperature and is at least the correct order of magnitude. We emphasize, however, that this is only a hypothesis and further experimentation in external magnetic fields may help clarify how the oxidation kinetics are modified at the Curie temperature.

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