Al(100), for example, produces useful amounts of thermally activated Ps at 500 K. Our results imply that the Ps from such a surface should have a velocity spread characteristic of this lower temperature. It is an exciting possibility that suitable surfaces could even be made to yield positronium with energy widths characteristic of cryogenic temperatures.

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Isothermal-Desorption-Rate Measurements in the Vicinity of the Curie Temperature for H_2 Chemisorbed on Nickel Films

M. R. Shanabarger
Quantum Institute, University of California, Santa Barbara, California 93106, and National Aeronautics and Space Administration, Ames Research Center, Moffett Field, California 94035

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Measurements of the net desorption rate for hydrogen chemisorbed onto nickel films in the vicinity of the Curie temperature are presented. Anomalies are interpreted in terms of anomalous variations in the absolute rate constants for the chemisorption reaction. The results are in qualitative agreement with Suhl's theory for the effect of second-order phase transitions on absolute rate constants.

It is known that the efficiency of reactions heterogeneously catalyzed at surfaces can be modified by bulk phase transitions of the catalyst. Several experimental observations of this phenomenon have been reviewed recently for magnetic catalysts.[1] The theoretical effort to understand this phenomenon had concentrated on the effect of ferromagnetic phase transitions on the rate constants of reaction steps for chemisorbed species.[2] A reaction step of particular interest is desorption from the chemisorbed state to the gas phase, since this can directly affect the overall efficiency of a catalyzed reaction. There has been, however, no detailed measurement of desorption rates in the vicinity of a ferromagnetic transition to compare with theory. An attempt to measure the isothermal desorption rate for H_2 chemisorbed onto Ni in the neighborhood of the Curie temperature was reported in an earlier work.[3] The measurements were, unfortunately, not internally reproducible.

In this note, I present new measurements of the isothermal desorption rate for H_2 chemisorbed onto polycrystalline Ni films. The measurements have been made over a temperature range that spans the Curie temperature of the Ni film, T_C^*. In the vicinity of T_C^* the measured net desorption rate, τ_d^{-1}, undergoes an anomalous decrease and the measured equilibrium constant for the chemisorbed hydrogen, K, displays a large increase. For temperatures above T_C^* the measured activation energy for the net desorption rate, E_d, appears to increase. It is known that the dissociative chemisorption of H_2 on Ni occurs via a molecular precursor.[4] At the temperature of these measurements, the path for desorption is via the precursor; hence, τ_d^{-1} is the result of the coupled dynamics (as represented by their respective rate constants) of the precursor and chemisorbed state. Analysis of the data shows that the rate constants for *both* the precursor and the chemisorbed state are modified in the vicinity of $T_C{}^*$ with the greater change occurring in the rate constants associated with the chemisorbed state. The changes in the rate constants are qualitatively consistent with theoretical predictions based on a spin coupling between the adatom and the magnetic substrate.[2] The fact that the precursor rate constants are changing suggests that an additional coupling mechanism is present, since the molecular precursor should not possess a net spin to couple with the Ni magnetization.

The measurements were made with thin Ni film adsorption substrates. Thin films were utilized for two reasons. First, the Curie temperature is significantly lower than that of the bulk metal.[5] At these lower temperatures the magnitudes of the thermally activated rate constants are in a more accessible range for isothermal measurements. Second, thin films permit the use of the chemisorption-induced resistance change[6] as a monitor of the kinetics. This technique has the sensitivity and dynamic range to adequately carry out isothermal hydrogen kinetic studies.

The films were produced *in situ* in an ultrahigh-vacuum environment by evaporation of high-purity Ni onto glass substrates; film dimensions are typically 25 mm × 3 mm. During evaporation, the substrate temperature, T_s, was maintained at 200 °C. After completion of the evaporation, T_s was increased to 300 °C for 1 h to anneal the film and stabilize its resistance.

The effective (conducting) film thickness was estimated from the room-temperature resistance corrected for finite-size effects[7]; typical values are 2.5–4 nm. Since the films are quite thin, $T_C{}^*$ is significantly reduced from the bulk value of 631 °K. $T_C{}^*$ was taken to be the temperature at which the anomaly in the temperature coefficient or resistance was a maximum. For these films, $T_C{}^*$ is approximately 500 °K, in good agreement with other studies.[6] Even though these films were annealed, $T_C{}^*$ shifted toward higher values with repeated temperature cycling, the maximum variation being about 5%.

The hydrogen coverage was determined by continuously measuring the chemisorption-induced change in resistance of the Ni film. The resistance change, δR, is directly proportional to the coverage of dissociated chemisorbed hydrogen.[4] For the desorption measurements, the initial coverage was typically less than 0.3 monolayer. The measurements were carried out isothermally; a thermocouple attached to the film substrate was used to measure and control the substrate temperature via suitable electronics.

The desorption kinetics were obtained by measuring the decay of δR after rapidly evacuating the gas-phase H_2 from an initial pressure of about 1.3×10^{-5}–1.3×10^{-4} Pa to pressures where readsorption was negligible ($\sim 6\times10^{-7}$ Pa). The adsorption process is reversible in the sense that δR returned to zero at the end of the desorption. The data are consistent with an exponential decay of δR at all temperatures. The reproducibility of τ_d^{-1} for a series of measurements is ± 12%. The measured net desorption rate, τ_d^{-1}, is taken to be the time constant of the exponential decay. Values of τ_d^{-1} in the vicinity of $T_C{}^*$ for a particular film are presented as an Eyring plot in Fig. 1. Different symbols are used to differentiate data taken initially while decreasing T_s after the annealing period from data taken later as T_s was increased from room temperature. The general behavior of τ_d^{-1} for $T_s < T_C{}^*$ for the data presented in Fig. 1 and for additional lower-temperature data not shown is in agreement

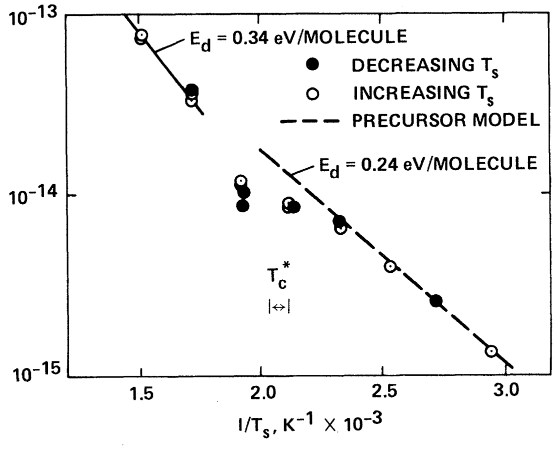

FIG. 1. Eyring plot of the net desorption rate, τ_d^{-1}, for H_2 chemisorbed onto a Ni film. Here h is Planck's constant and k_B is Boltzmann's constant. The range of Curie temperatures, T_C, due to thermal cycling of the film is indicated. The normal behavior would be for the data to follow the dashed line which is a fit to the precursor adsorption model in the absence of the ferromagnetic phase transition.

with data from thicker films. The deviation of τ_d^{-1} near T_C^* from that expected by extrapolation of the low-temperature data is quite evident in Fig. 1. In fact, it amounts to a decrease in τ_d^{-1} by a factor of 2. In addition, the activation energy for desorption, E_d (given by the slope of the data in the Eyring plot), appears to increase about 40% for $T_s > T_C^*$.

Resistance isotherms were recorded at several temperatures. The isotherms were analyzed by assuming them directly proportional to a Langmuir isotherm for dissociative adsorption with a coverage-independent equilibrium constant, K.[4] An excellent fit to the data was possible for estimated coverages up to 0.8 monolayer. The values of K are presented as an Arrhenius plot in Fig. 2. The typical analysis error in determining K is ± 30%. The expected temperature dependence of K based on other measurements is indicated by the solid line in Fig. 2. The value of K near T_C^* is about 2000 times greater than the expected value in the absence of the phase transition.

The dissociative chemisorption of hydrogen on Ni occurs via a molecular precursor. The reaction sequence is

$$H_2 + \Sigma^* \underset{k_d}{\overset{k_a p_{H_2}}{\rightleftharpoons}} (H_2\text{-}\Sigma^*) + 2\Sigma \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2(H\text{-}\Sigma) + \Sigma^*,$$

where $k_a p_{H_2}$ and k_d are, respectively, the absolute rate constants for adsorption and desorption between the gas phase and the precursor $(H_2\text{-}\Sigma^*)$; k_1 and k_2 connect the precursor with the chemisorbed state $(H\text{-}\Sigma)$; and Σ^* and Σ are physically distinct sites for the precursor and the chemisorbed state. Values for the rate constants for temperatures below T_C^* are presented in Table I. For temperatures above 250 °K, the desorption of chemisorbed hydrogen is bottlenecked by the step from the precursor state to the gas phase. Consequently, τ_d^{-1} is determined primarily by k_d.

The influence that variations in k_1 and k_2 have on τ_d^{-1} was evaluated from an approximate solution to the coupled nonlinear equations which describe the model.[8] The approximate solution agrees with *all* the data in the absence of the ferromagnetic phase transition and agrees, also, with exact numerical solutions of the complete model.[9] The approximate solution for τ_d^{-1} is indicated by the dashed line in Fig. 1 for $T_s < T_C^*$.

Numerical calculations show that τ_d^{-1} is given by $\tau_d^{-1} = k_d f(k_1/k_2)$ when k_d is reasonably constant. For the calculations, the frequency factors for k_1 and k_2 were changed several orders of magnitude while k_d's were varied only by a factor of 3. In the vicinity of T_C^*, the value of $f(k_1/k_2)$ is essentially unity for the expected values of the rate constants. The value of $f(k_1/k_2)$ near T_C^* changes slightly if k_1/k_2 is decreased. However, *an increase in the value of* k_1/k_2 *causes* $f(k_1/k_2)$ *(and, consequently,* τ_d^{-1}*) to decrease significantly.*

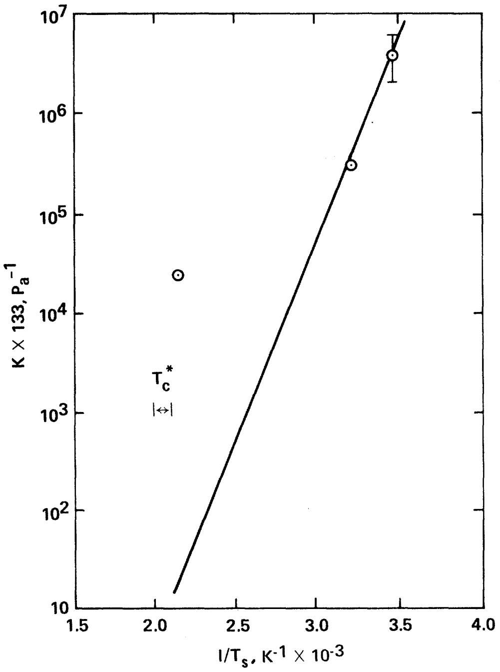

FIG. 2. The equilibrium constant, K, for H_2 chemisorbed onto Ni films. The behavior of K in the absence of the ferromagnetic phase transition is shown by the solid line.

TABLE I. Absolute rate constants for H_2/Ni chemisorption in the absence of the ferromagnetic transition.

$k_a = 1.5\times10^3$ (Pa sec)$^{-1}$;

$k_d = 0.0843T$(°K) $\exp(-E_d/k_BT)$ sec^{-1},
$E_d = 0.24$ eV/molecule;

$k_1 = 307T$(°K) $\exp(-E_1/k_BT)$ sec^{-1},
$E_1 \simeq 0.29$ eV/molecule[a];

$k_2 = 2.1\times10^{13}T$(°K) $\exp(-E_2/k_BT)$ sec^{-1},
$E_2 \simeq 0.83$ eV/molecule[a];

$K = [2.65\times10^{-7}/T$(°K)$]\exp(\Delta H/k_BT)$ Pa^{-1},
$\Delta H = 0.78$ eV/molecule.

[a] Estimated value.

Variations of k_d and k_1/k_2 near T_C* from their expected values were estimated by requiring that they be consistent with (1) the observed increase in K and (2) the observed decrease of τ_d^{-1}. Note that K for the precursor model is given by $K = (k_a/k_d)(k_1/k_2)$. For the data presented in Figs. 1 and 2, the analysis shows that k_d is reduced to 75% of its expected value with a relative uncertainty of ± 10%, while k_1/k_2 is increased by a factor of 1500 with a relative uncertainty of ± 20%. It has been assumed that k_a does not vary significantly near T_C*. If k_a does vary in the vicinity of T_C* then this will affect the value of k_1/k_2 (obtained from K) and, in turn, the value of k_d.

Recent calculations have demonstrated that anomalous changes in absolute rate constants can occur near bulk phase transitions if the degrees of freedom of the adsorbed species are coupled with the order parameter of the substrate. Suhl[2] has considered the specific example of exchange coupling between the spin on an adatom and the spin magnetization of a ferromagnetic metal substrate. He predicts that "adsorptionlike" rate constants will increase and "desorptionlike" rate constants will decrease in the vicinity of the ferromagnetic phase transition if the sign of the exchange coupling constant, A, is negative. In addition, the activation energy for desorption should increase for temperatures above the phase transition. The model applies only to k_1 and k_2 since they are associated with the dissociated chemisorbed state where it is possible for the hydrogen atom to spin couple to the Ni magnetization. Since k_1 is an "adsorptionlike" rate constant and k_2 a "desorptionlike" rate constant, then the predicted variations in k_1 and k_2 are such that the ratio k_1/k_2 will increase at the phase transition. This is in agreement with the data presented here. The observed change in k_1/k_2 is, however, several orders of magnitude larger than Suhl's estimates.

The precursor, being a molecular state, is not expected to have any significant spin coupling to the Ni magnetization. The decrease in k_d at T_C* and the increase in E_d for $T_s > T_C$* follow, however, the predictions of Suhl's model. In addition, Suhl argues that for $A < 0$, the maximum deviations should occur at a temperature somewhat higher than the bulk phase transition. Data in Fig. 1 seem to suggest that this is the case. The present data are not adequate, however, to establish this point firmly. The agreement between Suhl's model and the variations in k_d suggests that the precursor is coupled to the Ni magnetization. A possible coupling mechanism is the magnetoelastic energy of the Ni which should modulate the precursor's potential well. This would also contribute to the chemisorbed state and may produce larger variations in the rate constants when compared with the spin exchange coupling mechanism.

Finally, although the effect of the phase transition is to decrease the net desorption rate for the H_2/Ni system, it also increases significantly the population of the chemisorbed state (K increases). This will also result in the enhancement of the efficiency of a catalyzed reaction by increasing the concentration of the chemisorbed reactants.

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