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The Catalyzed o-pH_2 Conversion and Magnetocatalytic Effects on EuO and CrO_2

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Catalyzed *ortho-para*hydrogen conversion rates have been measured on both insulating and conducting types of europium monoxide over the temperature range 65–400 K. There was no rate anomaly in the neighborhood of the ferromagnetic–paramagnetic phase transition. A positive extrinsic field magnetocatalytic effect was observed in the paramagnetic phase but little effect was found below the Curie point. Chromium dioxide proved to be too reactive for measurements to be made near the Curie point. Catalytic activity was found, but no extrinsic field effect at room temperature. The theoretical implications of these results are discussed.

INTRODUCTION

The purpose of this work was to test a theoretical prediction concerning the expected change in catalyzed conversion rate for *ortho-para*hydrogen in the neighborhood of a ferromagnetic-paramagnetic phase transition. The conversion mechanism under consideration was physical (nondissociative) in all cases.

It has been shown (*1, 2*) that the o-$p$$H_2$ conversion rate on α-Cr_2O_3 undergoes a large decrease as the temperature is raised through the Néel point, 307 K. The second order phase transition in this case is from antiferromagnetic to paramagnetic, α-Cr_2O_3 $(a) \rightleftarrows \alpha$-$Cr_2O_3$ (p), and the rate change observed is an example of the Hedvall effect often found for catalyzed reaction rates at magnetic, and other, transitions. A clue to understanding such rate changes, insofar as they involve the magnetic o–$p$$H_2$ conversions, has been provided by Ilisca and Gallais (*3, 4*) who point out that, in a regular high surface density of spins, energy for the conversion may come from absorption or emission, as the case may be, of a spin wave. A development of this idea has been presented by Petzinger and Scalapino (*5*) who show that, if the effect is due to spin wave interactions (*6*), then near the phase transition the change of conversion rate with respect to temperature, $d\lambda_{II'}/dT$, should vary inversely as the Heisenberg exchange integral J_{exch} [Ref. (*5*), Eq. (90)]. For antiferromagnetic ordering $J_{\text{exch}} < 0$ and approaches zero as the temperature rises through the Néel point. A decrease of conversion rate is, therefore, predicted as the system undergoes magnetic disordering. This result is in agreement with experiment (*1, 2*).

For ferromagnetic ordering $J_{\text{exch}} > 0$. The Petzinger and Scalapino treatment predicts, therefore, that a transition under similar conditions with rising temperature through the Curie point will result in an increase of o–$p$$H_2$ conversion rate. It is this prediction that was tested in the present work.

The choice of a catalyst that may be used for the above purpose over the $X(f) \rightleftarrows X(p)$ transition is severely limited. In the Curie point region the catalyst must be stable in hydrogen, it must not show appreciable dissociative activity, and the Curie point must be sharply defined. It is a convenience if the catalyst lends itself to appropriate pretreatment for removal of adsorbed water vapor and other gases, and if the Curie point is not very much below

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room temperature. For gadolinium metal $T_c \simeq 298$ K. The o–pH$_2$ conversion over this metal has been studied by Eley and Norton (*7*). The conversion mechanism appears to be dissociative near T_c, and rapid reaction with H_2 obscures any Hedvall effect that may have been present. Another possibility is CrO_2, for which $T_c \simeq 394$ K. This was found to react rapidly with H_2 at T_c but the results of a few measurements at lower temperature are given. The most nearly satisfactory catalyst for the purposes of this work appears to be EuO, $T_c \simeq 70$–77 K. No previous measurements of catalytic activity on this oxide have been found. The relatively low Curie point presented some difficulties, none insurmountable.

It had previously been found (*1*) that α-Cr_2O_3 showed a decrease of catalytic activity just below the Néel point in magnetic fields of several MA·m^{-1}, (1 MA·m^{-1} = 12.6 kOe), and an increase above T_N. For that reason a few extrinsic field measurements were made of conversion rates on CrO_2 below T_c and on EuO both above and below T_c. For the latter substance it was necessary to use Gd-doped monoxide, with T_c in a more accessible region.

EXPERIMENTAL METHODS

Europium monoxide. The samples were obtained from International Business Machines Corp. through the courtesy of S. von Molnar and M. W. Shafer. One sample, here designated EuO(ins), was from the insulating, oxygen-rich part of the phase diagram (*8*) and contained Eu_3O_4 or Eu vacancies. The important property for the purposes of the present work was that the Curie temperature for this sample was within a degree of 69.3 K. Portions of the sample were ground to a black powder that proved to have a specific surface of 1.4 m^2·g^{-1} (BET, N_2). Sample weights used for catalytic measurements were 0.6 to 0.7 g. The Gd-doped sample, here designated EuO(con), was oxygen-poor and had a very high (metallic) electrical conductivity (*9*). The Curie temperature was 129 ± 3 K. Portions were ground to a surface of 0.8 m^2·g^{-1}. Sample weights used were 0.6 to 0.8 g.

The compound EuO is sensitive to moist air. A sample of the black powder started to turn green after a few seconds of exposure to the atmosphere. This change is doubtless due to surface oxidation and hydration. For that reason great care was taken to perform all operations in an atmosphere of pure, very dry helium. As an added precaution against surface oxidation the sample was heated to 773 K in flowing pure H_2 after it had been sealed into the reaction system, although it is not certain that this can reduce a surface layer of higher oxide.

Chromium dioxide. The sample, in the form of a black powder, was obtained from E. I. du Pont de Nemours and Co. through the courtesy of M. F. Bechtold and L. K. Jordan. This proved to have a specific surface of 28.5 m^2·g^{-1}. The Curie point was within a degree of 394 K. Sample weight used for catalytic measurements was 2.00 g. While this oxide is stable in air at room temperature it adsorbs, like all solids, water and other gases from the atmosphere. It was found that the p-H_2 conversion activity at 298 K was negligible for the untreated sample. But pretreatment in pure flowing helium with temperature slowly rising to 623 K produced a surface showing satisfactory activity at room temperature. This was achieved without any obvious change in appearance of the surface. However, in H_2 in the region of T_c, all activity was lost before any meaningful measurements could be made. This decay is doubtless due to surface reduction followed by adsorption of the water formed. For that reason all work on this substance was restricted to the ferromagnetic phase at, or near, room temperature.

Catalytic activities. All measurements were made in the flow reactor previously described (*10*) except that the solenoid used for applying a weak magnetic field was omitted. Hydrogen purified by palladium diffusion was passed over a converter to obtain o–p composition 3:1 or 1:1 as needed, then over the catalyst which was supported on a Vycor fritted disc.

Analysis of the exit gas was completed almost instantaneously in a 4-wire thermal conductivity cell calibrated continuously against equilibrated hydrogen. For the few magnetocatalytic measurements in the MA·m^{-1} region the reactor was placed in the gap of a 12 in. magnet. Temperatures in the range of 64.5–78 K were obtained by placing the reactor in pumped liquid nitrogen, monitored with a nitrogen vapor thermometer. The hydrogen flow rate through the reactor was about 0.8 cm^3·s^{-1} (STP) of initial o–p composition 3:1 or 1:1 as necessary. Proof that no appreciable dissociative activity was present was given by the virtual independence of conversion rate on temperature over the range of interest. Strong dissociative activity was observed above 400 K.

RESULTS

Specific o–pH$_2$ conversion rates for both preparations of EuO at various temperatures are given in Table 1. These results were obtained on several samples of catalyst and particular attention was given to the region of the Curie point. All measurements reported in Table 1 were made in zero extrinsic field except for the ambient Earth's field which showed, as expected for a catalyst of high surface site density, no measurable effect. Conversion rates (k_0) on a given sample were reproducible to ±10% provided that the measurements were completed within a few hours. On different samples of the same preparation agreement was obtained within a factor of two. Field effects $\Delta k = (k_H - k_0)/k_0$ where k_H is the conversion rate in a field of 1.4 MA·m^{-1} were reproducible to ±2% at 300 K, to ±10% at 78 K.

TABLE 1
SPECIFIC CONVERSION RATES, k_0[a]

Temp (K)	EuO (ins)	EuO (con)
64.5	2.3	—
65.1	1.8	—
67.1	1.9	—
68.6	1.9[b]	—
69.4	2.0[b]	—
70.2	2.0[b]	—
73	1.7	—
78	2.1	1.2
104	1.8	—
113	2.4	2.2
122	—	0.8[b]
133	—	1.3[b]
142	—	1.6
187	2.9	—
299	6.0	3.9
368	6.9	3.6

[a] Mol·s^{-1}·m^{-2} × 10^5.

[b] Approximate Curie temperature range.

TABLE 2
EXTRINSIC FIELD RESULTS ON EuO AND CrO$_2$

Sample	Temp (K)	$k_0 \times 10^5$ (mol·s^{-1}·m^{-2})	$\Delta k \times 10^2$
EuO(ins)	300	6.0	+46
	78	2.1	+24
EuO(con)	300	3.9	+40
	78	1.2	<10
CrO$_2$	298	0.12	<0.5

Results of the extrinsic field effect are shown in Table 2, which includes data on both forms of EuO and also on CrO$_2$. Because of the reasons described above all work on CrO$_2$ was limited to a rate determination and field effect at room temperature.

DISCUSSION

There do not appear to have been any previous catalytic rate studies on EuO or CrO$_2$. It is, therefore, of interest to compare the o–pH$_2$ conversion rates on these substances with those on closely related compounds. The specific rate at 299 K on EuO(ins) is given in Table 1 as 6.0 × 10^{-5} mol·s^{-1}·m^{-2}. The Gd^{3+} ion is isoelectronic with Eu^{2+}. Two earlier rate results (*10, 11*) on Gd$_2$O$_3$ under similar conditions were 3.5 × 10^{-4} and 1.7 × 10^{-4}. Two results on Eu$_2$O$_3$ were 2.6 × 10^{-4} and 1.6 × 10^{-4}. The difficulties involved in the comparison of specific rates over different solids are well known. We cannot say with certainty that the rate over EuO is low by about one order, but the possibility of surface contamination cannot be excluded. We cannot say with certainty that the previously reported rate over Eu_2O_3 is not high by about one order because of some surface reduction of Eu^{3+} to Eu^{2+} with consequent increase of magnetic moment.

The specific rate on CrO_2 at 298 K is given here as 1.2×10^{-6} $mol \cdot s^{-1} \cdot m^{-2}$. The rate previously given (*2*) for α-Cr_2O_3 just below the Néel point was about 1.0×10^{-3}. This large difference is reasonable because Cr^{4+} has a smaller moment that Cr^{3+}, the oxide ion concentration is higher in CrO_2, and the pretreatment given the Cr_2O_3 (H_2 at 773 K) almost certainly exposes the chromium ions directly on the surface with a probable reduction to Cr^{2+} which has a still higher moment (*12*).

With respect to the main purpose of this work it may be said that in the neighborhood of the transition $EuO(f) \rightleftarrows EuO(p)$ there is no fractional change of conversion rate greater than about ±10%. This applies to both the insulating, and the conducting, phases of EuO. A change of rate over EuO near T_c would have confirmed the success of the Petzinger and Scalapino theoretical treatment for the transition α-Cr_2O_3 $(a) \rightleftarrows \alpha$-$Cr_2O_3$ (p). But failure to find a rate change may be related to the much lower T_c for EuO as compared with that of Cr_2O_3. The spin wave correlation is based on the assumption that the spin dynamics is *slower* than the molecular diffusion rate, and this is crucial for the succeeding argument. In view of this it is possible that a better approximation to the conversion rate change near T_c for EuO would be Petzinger and Scalapino's Eq. (82) (*5*) in which diffusion is treated as small in comparison with spin motion. If this is the case then the conversion rate depends on factors that are varying only slowly around T_c.

It did not prove possible to measure the extrinsic field effect on EuO(ins) in the ferromagnetic phase. But both samples of EuO in the paramagnetic phase showed a positive field effect in the $MA \cdot m^{-1}$ region as has been the case for all catalysts thus far studied, provided that these have a high concentration of spin sites. If any field effect occurs for EuO(con) in the $MA \cdot m^{-1}$ region and below T_c it is quite small. The change from an insulating to a conducting catalyst (a change of about 10^6 in conductivity) had no effect on the conversion rate although it had been thought that some difference in rates, especially as measured moderately above room temperature, might have been found. It did not prove possible to measure the extrinsic field effect on CrO_2 in the paramagnetic phase. This oxide in the ferromagnetic phase showed conversion activity but no measurable field effect. Ilisca and Gallais (*4*) have attempted to explain the extrinsic field effect on ferromagnetic catalysts by reference to orientation of the surface magnetization. But no experimental demonstration of such an effect has ever been verified. The results of Justi and Vieth (*13*), quoted by Ilisca and Gallais, have been disputed by Schwab and Kaiser (*14*) and, in any event, referred to the dissociative mechanism for the o–pH_2 conversion over activated nickel metal. There is no conflict between those results and the ones reported here. Our final conclusion must, therefore, be that no theoretical basis for the extrinsic field magnetocatalytic effect has yet been found.

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