

Hydrogen Reduction of Ruby at High Pressure: Implication for Claims of Metallic Hydrogen

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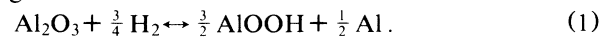
We show that the reaction $\text{Al}_2\text{O}_3 + \frac{3}{4}\text{H}_2 \leftrightarrow \frac{3}{2}\text{AlOOH} + \frac{1}{2}\text{Al}$ proceeds to the right at 300 K and at pressures above 136 GPa, producing the metal aluminum in the process. The system of neighboring particles of Al_2O_3 coated with aluminum hydroxide oxide and covered with aluminum is a dc conductor and exhibits a resonance in the infrared which appears as a plasma edge. In view of this, claims of production of metallic hydrogen based on reflectivity studies on composite $\text{Al}_2\text{O}_3\text{-H}_2$ samples are unwarranted.

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Mao, Hemley, and Hanfland¹ have reported reflectivity results on three samples of hydrogen at high pressure which they interpret as indicating metallization of hydrogen at 149 GPa. Two of their samples contained 5% ruby powder (initial volume) and were pressurized to 172 and 177 GPa. (Note that a 5% initial volume of Al_2O_3 at 0.3 GPa becomes 26% by volume at 170 GPa.) They show reflectivity data at 172 GPa for one of these samples and data for four pressures (142, 158, 167, and 177 GPa) for the other. Both experiments showed reflectivity increases of several percent in the infrared. They also show results at 161 GPa for the remaining sample which contains only a small amount of ruby powder, and which shows interference fringes. It is likely that the results of the 161-GPa experiment are due to a combination of regions of composite and regions of hydrogen only.

Using the values of $\hbar\omega_p$, \hbar/τ , and ϵ_{1B} given at 159 and 167 GPa by Mao, Hemley, and Hanfland¹ based on their composite $\text{Al}_2\text{O}_3\text{-H}_2$ samples, and interpolating linearly with pressure, the values at 161 GPa are 1.31 eV, 0.683 eV, and 13.4, respectively. These Drude parameters give a linear absorption coefficient of $\mu = 1.83 \mu\text{m}^{-1}$ for an arbitrarily assumed energy in the infrared of $\hbar\omega = 0.683$ eV. (From elasticity calculations, if the diamond anvils are touching at the bevel edge, their spacing in the middle is still $1.5 \mu\text{m}$.) Thus a $2\text{-}\mu\text{m}$ -thick sample (a reasonable minimum thickness) would give on two passes $I/I_0 = 0.0007$ for the assumed energy noted; therefore, the low-energy portion of the fringe pattern seen in their Fig. 1(a) at 161 GPa should not be observable. The actual expected fringe pattern has been calculated *in detail* with the same conclusion.² In addition, no absorption or reflection increases in the infrared were found² in experiments without alumina powder although an isolated ruby chip was present but was not involved in the area of the sample studied. We conclude that there is a basic inconsistency in the interpretation between the two types of experiments; those with large amounts of Al_2O_3 powder (and interpreted as showing Drude reflectivity) and that with little Al_2O_3 powder (and showing Fabry-Pérot fringes and behavior which was interpreted as Drude reflectivity).

In order to explain the reflectivity data we consider the possibility of reaction of the strong reducing agent hydrogen with an oxide as follows:



At 298.15 K and 1-atm pressure the Gibbs-free-energy change for this reaction^{3,4} is 200.94 kJ/mol. We use $\Delta G_{300}^0 = 201.1 \pm 0.1$ kJ/mol at 300 K and atmospheric pressure (i.e., gaseous hydrogen) in the calculations which follow. Thus under these conditions, alumina and hydrogen are the stable phases. At high pressure

$$\Delta G(P) = \Delta G_{300}^0 + \int_{1 \text{ atm}}^P (V_p - V_r) dP. \quad (2)$$

Here V_p is the volume of the products and V_r is the volume of the reactants at a pressure P . In order to evaluate this ΔG it is necessary to know the equations of state at 300 K of the four materials.

Al₂O₃.—It is known that the α -alumina structure of Al_2O_3 persists at room temperature to the highest pressures studied, 170 (Ref. 5) and 201 GPa.⁶ The equation of state measured to 170 GPa can be fitted with the Birch I equation:

$$P = \frac{3}{2} B_0 (x^{7/3} - x^{5/3}) [1 + 0.75(B_0' - 4)(x^{2/3} - 1)]. \quad (3)$$

Here $x = V_0/V$, where V_0 is the molar volume at zero pressure and V is the molar volume at pressure P , and B_0 is the value of the bulk modulus at zero pressure and B_0' is the value of the pressure derivative of the bulk modulus at zero pressure. We use $V_0 = 25.60 \times 10^{-6} \text{ m}^3/\text{mol}$, $B_0 = 254$ GPa, and $B_0' = 4.3$.⁵ We expect P for a given V to be accurate to 3%.

Hydrogen.—At low pressures the P - V results of Michels *et al.* are used.⁷ Between 0.2 and 2.25 GPa, the data of Mills *et al.* are used.⁸ Above 5.4 GPa, hydrogen is solid at room temperature and excellent x-ray data are available to 26.5 GPa where the molar volume is $7.992 \times 10^{-6} \text{ m}^3/\text{mol}$.⁹ Thus the fitted equation of state of Ref. 9 is used in this regime. In the region between 2.25 and 5.4 GPa a Birch I [Eq. (3)] fit to the data of Mao *et al.*⁹ is used. At pressures above 26.5 GPa the fit to data used by Ashcroft¹⁰ is rewritten in the form

$$V \left[\frac{\text{m}^3}{\text{mol}} \right] = 4.791 \times 10^{-6} \left[\frac{26.5}{P(\text{GPa})} \right]^{1/2.9}. \quad (4)$$

Raman studies suggest a transformation of hydrogen in the neighborhood of 150 GPa, possibly an orientational-ordering transformation.^{11,12} Such transformations are important as they could involve a discontinuous decrease in volume and hence upset our free-energy calculations. However, we point out that even a very large fractional volume change of 5% of H₂ at 150 GPa would cause only a change of volume of 0.1×10^{-6} m³/mol Al₂O₃ and so would not cause a major error in the ΔV of the reaction which is $\Delta V = V_p - V_r = -1.54 \times 10^{-6}$ m³/mol Al₂O₃ at this pressure, as we will see later. Except for this we expect P to be accurate for a given V to 4%.

AlOOH.—This hydroxide has two polymorphs which exist at atmospheric pressure in bauxite, namely, boehmite and diasporite.¹³ Diasporite is slightly denser with $V_0 = 17.76 \times 10^{-6}$ m³/mol. Our measured value of B_0 for diasporite is $B_0 = 85$ GPa. We use $B'_0 = 5.2$ for diasporite, the value found experimentally¹⁴ for Ca(OH)₂, the only hydroxide for which we could obtain data. Any transition of diasporite would tend to decrease the volume of this product and hence would make the volume of the reaction even more negative and would reduce the pressure at which $\Delta G = 0$. Except for this possibility we expect the P for a given V to be accurate to 4%.

Aluminum.—We use $V_0 = 9.993 \times 10^{-6}$ m³/mol, $B_0 = 72.9$ GPa, and $B'_0 = 5.15$ in the Birch I equation.¹⁵ We know from unpublished experimental work in our laboratory that the fcc structure of aluminum persists to at least 150 GPa. We expect P for a given V to be accurate to 3%.

Table I shows the computed volumes for the four components of the reaction, the net volumes (products minus reactants), and the total Gibbs-free-energy change for reaction of one mole of Al₂O₃ at 300 K. At $P = 136$ GPa, $\Delta G = 0$. At higher pressures the formation of aluminum metal is thermodynamically favored.

When Al is formed the possibility of forming AlH₃ also has to be considered. At atmospheric pressure this reaction is only slightly favored; at pressures above 1 atm it initially becomes more favored, but at higher pressures it becomes less favored and in the submegabar regime and higher the compound is unstable.

We expect a layer of Al to form on top of a layer of AlOOH on the surface of the Al₂O₃ particles. The most highly reduced material would be next to the reducing agent, hydrogen, followed by the partially reduced AlOOH with the most oxidized alumina being furthest from the reducing agent. The reduction of the highest

TABLE I. Pressure, volumes, volume of reaction, molar Gibbs free energy of hydrogen, and Gibbs free energy of reaction. Volumes are in cm³. $(G^P)_{H_2}$ is the Gibbs free energy per mole of hydrogen.

P (GPa)	$1.5 V_{AlOOH}$	$.5 V_{Al}$	$V_{Al_2O_3}$	$.75 V_{H_2}$	$(V_p - V_r)$	$(G^P)_{H_2}$ (kJ)	ΔG^P_f (kJ)
0.000102	26.64	4.99	25.57	18520.	-18514.	0.000	201.100
10.0	24.29	4.50	24.66	5.02	-0.89	115.903	163.966
20.0	22.78	4.19	23.89	3.96	-0.87	174.635	155.553
30.0	21.68	3.98	23.23	3.44	-1.02	223.655	146.120
40.0	20.81	3.81	22.65	3.12	-1.15	267.252	135.243
50.0	20.10	3.67	22.14	2.89	-1.26	307.204	123.173
60.0	19.49	3.55	21.67	2.71	-1.34	344.474	110.181
70.0	18.97	3.45	21.25	2.57	-1.40	379.650	96.492
80.0	18.52	3.37	20.87	2.45	-1.44	413.130	82.278
90.0	18.11	3.29	20.52	2.36	-1.48	445.193	67.672
100.0	17.74	3.22	20.19	2.27	-1.50	476.047	52.774
110.0	17.41	3.16	19.89	2.20	-1.52	505.854	37.662
120.0	17.11	3.10	19.60	2.13	-1.53	534.739	22.398
130.0	16.83	3.05	19.34	2.08	-1.54	562.805	7.033
140.0	16.57	3.00	19.09	2.02	-1.55	590.136	-8.398
150.0	16.33	2.95	18.85	1.98	-1.55	616.801	-23.863
160.0	16.10	2.91	18.63	1.93	-1.55	642.859	-39.337
170.0	15.89	2.87	18.41	1.89	-1.55	668.362	-54.800
180.0	15.69	2.83	18.21	1.86	-1.54	693.352	-70.237
190.0	15.50	2.80	18.02	1.82	-1.54	717.867	-85.362
200.0	15.33	2.77	17.84	1.79	-1.53	741.942	-100.977

iron oxide forms such a sequence.¹⁶ The aggregate of particles touching each other in the present case would be a dc conductor. At high pressures the sample is 26% Al₂O₃; however, sedimentation of the sample contacting the diamond at which reflection occurs creates a settled aggregate of Al₂O₃ particles, perhaps 60% by volume with hydrogen present at 40% volume. If at high pressure the reaction were to go to completion (see Table I), there would be about 9% Al (by volume), 51% AlOOH, and 40% H₂. We would not expect the reaction to go to completion so the amount of Al present could increase as the pressure increases (larger driving force, longer time) resulting in a higher reflectivity at high pressures. The sample might be considered as a packing of Al-coated spheres (which are touching) in a composite dielectric with a dielectric constant ϵ_1 (real). The size of the spheres ($\sim 0.1 \mu\text{m}$) is small compared to the wavelength where reflectivity changes are observed ($\sim 2 \mu\text{m}$). Thus a wave sees an effective electron density $n_e = n\eta$, where n is the electron density of the fully dense metal at pressure and η is the volume fraction of metal in the composite. The presence of the nonmetal dielectric (Al₂O₃, AlOOH, and H₂) effectively decreases the electron density by η and in the same way decreases the plasma frequency by

$$\omega_{ep}^2 = \omega_p^2 \eta. \quad (5)$$

Thus this geometry with $\lambda \gg d$, where d is the particle size, leads to an effective dielectric constant

$$\epsilon_e = \epsilon_1(1 - \eta) + \epsilon_M \eta, \quad (6)$$

where ϵ_1 is the effective dielectric constant of the insulator and ϵ_M is the dielectric constant of the metal. We have modeled this metal-insulator combination with a one-dimensional stratified-layer model, with layers of metal of random thickness (with an average of 7 Å) and with alternating layers of insulator of random thickness and obtain exact solutions for this. We find that the volume-fraction relation of Eq. (6) holds fairly closely. This will be described in a separate paper. Since we are concerned only with the behavior in the infrared, we ignore the interband transitions which are present in the visible in aluminum. We, therefore, model the aluminum as a Drude metal:

$$\epsilon_M = \left[1 - \frac{\omega_p^2}{\omega^2 + \Gamma_p^2} \right] + i \frac{\omega_p^2 \Gamma_p}{\omega(\omega^2 + \Gamma_p^2)}. \quad (7)$$

At 177 GPa, $\hbar\omega_p = 20.96$ eV. Thus from (6) and (7), it follows that

$$\epsilon_e = [\epsilon_1(1 - \eta) + \eta] - \frac{\omega_{ep}^2}{\omega^2 + \Gamma_p^2} + \frac{i\omega_{ep}^2 \Gamma_p}{\omega(\omega^2 + \Gamma_p^2)^2}. \quad (8)$$

We use the pressure dependence of relaxation times in aluminum of Dandrea and Ashcroft.¹⁷ From their data points at $P=0$ and 31 GPa, we obtain

$$\hbar\Gamma_p = 0.184 + 0.9296(\rho_{m0} - \rho_m)/\rho_{m0}, \quad (9)$$

where ρ_m is the mass density and ρ_{m0} is the mass density at atmospheric pressure. At 177 GPa, $\rho_m/\rho_{m0} = 1.757$

and $\hbar\Gamma_p = 0.89$ eV. This value of Γ_p for Al compares favorably with the value of 0.77 eV obtained by Mao, Hemley, and Hanfland¹ at this pressure. The value of Γ_p expected for hydrogen is more than an order of magnitude less. From the method of Stevenson and Ashcroft,¹⁸ the resistivity of liquid metallic hydrogen calculated for 177 GPa and 300 K (where the liquid is metastable) is $1 \times 10^{-8} \Omega\text{m}$, so for solid hydrogen $\rho \approx 0.5 \times 10^{-8} \Omega\text{m}$. It follows from the Drude relation and Eq. (4) that $\hbar\Gamma_p = 0.02$ eV. Hydrogen still shows nicely separated R_1 and R_2 ruby peaks even at 230 GPa;¹⁹ thus the shear stresses must be small and the deformation defects mostly annealed. It is doubtful if an increase of resistivity by a factor of 3 or 4 as occurs in a shock experiment²⁰ would be present and would cause $\hbar\Gamma_p$ to rise to 0.077 eV, still a factor of 10 from that observed by Mao, Hemley, and Hanfland.¹ Thus the experimental Γ_p value is consistent with that for Al but is totally inconsistent with that expected for hydrogen.

With $\eta = 0.0133$ (which gives $\hbar\omega_p = 2.42$ eV) and with 60% of the volume initially occupied by Al₂O₃ (assumed to be spheres of radius 1000 Å) the surface thickness of aluminum is only 7.4 Å. We might consider the possible kinetics of the reaction in Eq. (1). We know that coherent oxide films form extremely rapidly (seconds) on clean aluminum at room temperature.²¹ There seems to be no reason why the reverse of the reaction, Eq. (1), should not be equally fast. Since the regrowth needed is so small, it is likely that it is epitaxial. In our studies on oxygen²² we found that it reacts much more rapidly with stainless-steel gaskets at very high pressure than at atmospheric pressure, producing oxides with a thickness of several micrometers. Also, dry fluorine does not attack diamond anvils at atmospheric pressure or even at about 1 GPa at room temperature, but it attacks diamond very strongly beginning at pressures of about 3 GPa, forming CF₄ in the process at room temperature.²³ So, reaction rates in the megabar-pressure regime can be fast at room temperature.

The quantity in brackets in Eq. (8) can simply be set equal to the value of ϵ_{1B} used in Ref. 1. (This is a parameter which depends strongly on the refractive index assumed for diamond since the studies involve reflection at the diamond-composite interface.) We see that the experimental data of the Al₂O₃-H₂ composite is consistent with touching spheres, coated with aluminum (1.33% by volume), with the relaxation time near that expected for aluminum. Thus the composite experiments (high Al₂O₃) are consistent with a strong reflectivity due to Al while the experiment with only a little Al₂O₃ can be interpreted as follows: There are open regions with pure H₂ which gives the fringes and there are composite regions (initially Al₂O₃+H₂) which give a rising reflectivity due to the Al created there. Since we calculate that Al formation can begin at 136 ± 20 GPa (very close to the 149 GPa at which Mao *et al.* saw reflectivity increase in their Al₂O₃-H₂ composite sample), claims of

production of metallic hydrogen seem at least ambiguous at this time.

While this paper was in preparation we were informed of a paper on hydrogen² which from analysis of absorption and reflection data shows no evidence of metallization to 230 GPa, consistent with the conclusion reached here. Inasmuch as pressures as high as 416 GPa have been achieved recently [measured by sound scientific procedures (x-ray diffraction)]²⁴ it is still conceivable that it will be possible one day to produce even monatomic metallic hydrogen in the diamond-anvil cell. However, it should be noted that just because pressures of 416 GPa can be obtained on a molybdenum sample placed in a drilled sample hole in a spring-steel gasket, it does not follow that such pressures will be attainable with hydrogen. Moreover, it is not clear that analytical studies can be made.

In conclusion:

(1) The reduction of alumina by hydrogen to produce metallic aluminum is thermodynamically favored above 136 GPa.

(2) If the reflectivity data obtained on the Al₂O₃-H₂ composite are due to a change of the optical properties of hydrogen (represented by a Drude model), then no interference fringe should be observable at low energies in the sample at 161 GPa with only a small amount of Al₂O₃ powder. But such fringes are observed. Hence the optical difference must be due to some other change in the composite.

(3) The reflectivity in all the samples can be explained on the basis of the presence of 7.4-Å layers of Al. In the case of the samples with a small amount of Al₂O₃ initially, the simultaneous presence of a small reflectivity rise and fringes can be explained as regions with only H₂ give the fringes while regions with both Al₂O₃ and H₂ give reflectivity again due to Al.

(4) Moreover, the fact that the experimental reciprocal relaxation time term, $\hbar\Gamma_p$, is consistent with that for aluminum but an order of magnitude larger than that expected for even heavily plastically deformed hydrogen is also consistent with aluminum being present in the Al₂O₃-H₂ composite material so that Al is the most likely candidate for the reflectivity results seen in Ref. 1.

(5) Therefore, the assumption that reflectivity increases in the infrared of the Al₂O₃-H₂ composites at high pressures are due to the production of metallic hydrogen is unjustified.

(6) There is, therefore, no evidence from reflectivity or absorption studies that metallic hydrogen has been produced.

(7) Inasmuch as pressures as high as 416 GPa have been achieved in the diamond-anvil cell,²⁴ it is conceivable that even monatomic metallic hydrogen can be made though it may be with great difficulty.

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