

LETTER TO THE EDITOR

Dense Hydrogen and Disproportionation

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Stabilization of a spontaneous polarization of the H₂ molecules rather than of the monatomic metallic state at ultrahigh pressures (~250 GPa) is contrasted with stabilization of the disproportionation reaction 2 Bi(IV) = Bi(V) + Bi(III) in BaBiO₃.

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Hydrogen, the lightest element, is known for its anomalous chemical behavior. Although it is generally placed in the first group of the periodic table along with the alkali metals because of its 1s¹ electronic configuration, hydrogen is not metallic in the solid state. However, it was predicted, first by Wigner and Huntington (1) more than 60 years ago, that molecular hydrogen would dissociate under high pressure to form a monatomic metallic solid similar to the alkali metals. In view of subsequent predictions that such a “metallic” hydrogen would exhibit a number of exotic properties, including high-temperature superconductivity (2, 3), the metallization of solid hydrogen has been a holy grail for high-pressure researchers (4). Intriguingly, however, despite the availability of pressures far in excess of the predicted pressure (25 GPa) required for the metallization of hydrogen, a metallic state for hydrogen remains elusive today (4, 5).

Hydrogen stays in the molecular state in its three solid phases, Fig. 1. In phase I the H₂ molecules freely rotate and in phase II they only librate. Phase III, which exists only above 160 GPa, is the most intriguing. Not only does hydrogen remain in a molecular form in this insulating phase up to the highest pressures yet applied; it also exhibits infrared absorption (6) and spontaneous polarization (7). Although the spontaneous polarization of the H₂ molecule into H^{δ+}–H^{δ-} in phase III has recently been calculated (7) to be δ ≈ 0.03, nevertheless it is instructive to contrast the onset of a spontaneous polarization in dense hydrogen with the stabilization of a “negative-U” charge-density wave, i.e., disproportionation, in a perovskite such as BaBiO₃.

The two-electron ground-state wave function for the H₂ molecule is

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = [u_1(1)u_2(2) + u_2(1)u_1(2)][\alpha(1)\beta(2) - \alpha(2)\beta(1)],$$

[1]

where $u_1 = c_{11}\phi_a + c_{12}\phi_b$, $u_2 = c_{21}\phi_a + c_{22}\phi_b$, and ϕ_a, ϕ_b are the atomic 1s wavefunctions for H atoms A and B of the molecule. The second factor in Eq. [1] refers to the singlet spin state. The first factor may be rewritten as

$$[\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)] + \mu[\phi_a(1)\phi_a(2) + \phi_b(1)\phi_b(2)]$$

[2]

where $\mu \equiv 2\lambda/(1 + \lambda^2)$ and $\lambda \equiv c_{12}/c_{11} = c_{21}/c_{22}$. In molecular orbital (MO) theory, the polar terms are admixed equally with the nonpolar terms ($\lambda = 1$), but in the Heitler–London model $\lambda < 1$ is assumed. Coulson and Fischer (8) have calculated $\lambda \approx 1/8$ at the equilibrium separation R_0 of the H atoms in the H₂ molecule. This result says that the Mott–Hubbard (9, 10) energy U required to put two electrons on the same atom is large enough to reduce μ from the value $\mu \approx 1$ assumed in MO theory to $\mu \approx 0.25$.

The formation of metallic hydrogen at atmospheric pressure would require the sharing of bonding electrons with several near neighbors, which would increase R_0 between nearest neighbors and reduce μ even further. It follows that the width W of the 1s band of metallic hydrogen at atmospheric pressure would be narrow relative to the energy U required to create H⁺ and H⁻ ions. In the absence of energetically accessible p states, the narrow H1s band would be half-filled. Such a narrow band would be unstable relative to transitions that stabilize occupied states at the expense of empty states. By analogy with narrow d bands in transition-metal oxides, three such transitions are these: (1) dimerization to form H₂ molecules that are bonded by weak van der Waals forces, (2) formation of localized H: 1s¹

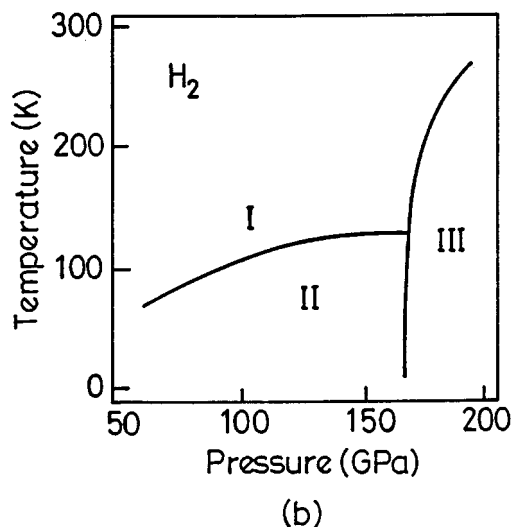


FIG. 1. Phase diagram of hydrogen at high pressure (schematic).

configurations that are bonded by weak superexchange interactions, and (3) disproportionation into $H^-:1s^2$ and $H^+:1s^0$ ions that are strongly bonded by an electrostatic Madelung energy $E_M > U$.

In the absence of steric constraints that restrict reduction of the interatomic separation, we can rule out the second of these alternatives, i.e., an antiferromagnetic coupling between localized spins, and the relatively large value of U makes the ionic alternative less stable than the formation of diatomic molecules.

In phase III hydrogen, high pressure reduces the intermolecular separation by a factor of 9, which forces much stronger intermolecular interactions than the weak van der Waals bonding formed at atmospheric pressure. These interactions are not merely steric, reducing the libration of the molecules; they also enhance the intermolecular virtual electron transfer represented by the admixture of $H_2^{n+} + H_2^{n-}$ polar states into the ground state as a result of the increased overlap of the empty antibonding and filled bonding orbitals on neighboring H_2 molecules. We denote the electron–electron coulomb energy for this transfer as U_m . These charge transfers reduce the splitting between the antibonding and bonding orbitals to give a positive feedback; and at a critical intermolecular separation, the system can be expected to become metallic, perhaps remaining diatomic, with a bandwidth $W > U_m$. The observation of phase III solid hydrogen indicates stabilization of an intermediate transition to a phase with spontaneous polarization of the H_2 molecules.

Spontaneous polarization of the H_2 molecules to $H^{\delta+}-H^{\delta-}$ involves biasing of the polar terms in Eq. [2] away from atom A toward atom B by an internal electric field, which would be a crystalline field set up by the

cooperative polarization of neighboring molecules. Such cooperative polarization would further reduce the splitting between bonding and antibonding states, thereby enhancing the intermolecular bonding by virtual intermolecular charge transfer as well as by introducing modest Madelung stabilization. The virtual intermolecular charge transfer would be from an $H^{\delta-}$ atom on one molecule to the $H^{\delta+}$ atoms on neighboring molecules. With increasing pressure, this intermolecular bonding must increase, which raises the following question: Will the polarization of the molecules increase until the intramolecular and intermolecular distances are equal, which would correspond to an ionic lattice with virtual charge transfer from H^- to H^+ ions representing a strong covalent component of the bonding, or will the system become metallic before this limit is reached? Since U is relatively large and the driving force for the spontaneous polarization is the intermolecular virtual electron transfer, a metallic state with real charge transfer and $W > U_m$ would be more stable than the ionic state in ultradense solid hydrogen.

Comparison of this situation with the observation (11) of a disproportionation of Bi(IV) into Bi(V) and Bi(III) in the perovskite $BaBiO_3$ is instructive. In the perovskite, the $BaBiO_3$ array of corner-shared octahedra contains $(180^\circ - \phi)$ Bi–O–Bi interactions, and a $Bi6s$ band would be half-filled. The larger radial extension of the $6s$ electrons relative to the $1s$ electrons reduces the energy U required to create polar states by the electron transfer $6s^1 + 6s^1 \rightarrow 6s^0 + 6s^2$. Moreover, the Bi–O–Bi interactions are too strong to stabilize antiferromagnetic coupling between localized spins $s = 1/2$. In the absence of Bi–Bi interactions, stabilization of occupied states at the expense of empty states near the Fermi surface of a half-filled $Bi6s$ band can only be accomplished either by condensation of superconductive Cooper pairs or by the disproportionation reaction $2Bi(IV) \rightarrow Bi(V) + Bi(III)$. A long-range-cooperative disproportionation reaction of this type is referred to as a “negative U ” charge-density wave (CDW) in the physics literature. However, in this case the driving force for the disproportionation reaction is not the Bi–O–Bi electron-transfer interactions, but the Bi–O interactions. Cooperative displacement of the oxygen atoms along the Bi–O–Bi bond axes to create six short Bi–O bonds on alternate Bi atoms and six long Bi–O bonds on the other half of the Bi atoms is possible in the perovskite structure. These displacements raise the energies of the antibonding $6s$ states at the sites with shorter Bi–O bonds; they lower these energies at the sites with longer Bi–O bonds. Therefore, the oxygen displacements induce electron transfer from the sites with shorter bonds to those with longer bonds. Here the oxygen displacements stabilize disproportionation into Bi(V) and Bi(III) whereas the Bi–O–Bi interactions would stabilize a metallic state. In the case of hydrogen, there are only H–H interactions.

The “negative- U ” CDWs stabilized at low temperatures in the transition-metal perovskites CaFeO_3 and NdNiO_3 are also instructive. In each of these compounds, the π -bonding $3d$ orbitals from localized t^n configurations whereas stronger $M\text{--O}$ σ -bond covalency makes the $(180^\circ - \phi)$ $M\text{--O--M}$ interactions transform the σ -bonding $3d$ orbitals into a narrow, antibonding σ^* band of itinerant-electron states having an e -orbital parentage. Above room temperature, the iron ions of CaFeO_3 are in their high-spin $\text{Fe(IV)}:t^3\sigma^{*1}$ state. In both oxides, the twofold e -orbital degeneracy reduces the electrostatic energy U required for a disproportionation of the σ^{*1} electrons into localized e^2 configurations and molecular σ^{*0} configurations, but each compound transfers electrons to the empty e orbitals in a different way. Mössbauer measurements of CaFeO_3 indicate a progressive cooperative displacement of oxygen away from Fe_I toward Fe_{II} atoms with decreasing temperature below a smooth transition at 290 K. Longer $\text{Fe}_I\text{--O}$ bonds stabilize $\text{Fe}_I\text{--}e$ orbitals and shorter $\text{Fe}_{II}\text{--O}$ bonds destabilize molecular Fe_{II}O_6 cluster orbitals until, at lowest temperatures, localized $\text{Fe}_I(\text{III}):t^3e^2$ configurations coexist with molecular complexes $\text{Fe}_{II}(\text{V})\text{O}_6:t^3\sigma^{*0}$ (12). In NdNiO_3 , on the other hand, the antiferromagnetic order below a first-order transition at $T_1 = 200$ K corresponds to a cooperative electron transfer from $\text{O}p_\sigma$ orbitals on alternate (111) NdO_3 planes to empty $\text{Ni--}e$ orbitals to stabilize more covalently bonded $\text{Ni(II)--(NdO}_3\text{)--Ni(II)}$ (111) layers separated by

more ionic $(\text{NdO}_3)^{3-}$ planes (13). In each of these cases, the oxygen atoms play a key role in the stabilization of a “negative- U ” CDW.

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