Does metallic ammonium exist? (From old and new literature)

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In many respects the behavior of the ammonium ion, NH_4^+, is that of an alkali metal ion. The radius of the NH_4^+ ion in a crystal (1.43 Å) is very close to the corresponding radii of potassium (1.33 Å) and rubidium (1.44 Å). Many ammonium salts form solid solutions with the corresponding potassium and rubidium salts.

Ammonium also forms amalgams with mercury, which can be thought of as alloys of hypothetical metallic ammonium. These amalgams eventually decompose by the reaction

$$2NH_4Hg \rightarrow 2NH_3 + H_2 + 2Hg.$$

No metallic ammonium in the free state has been observed, however.

In the electrolysis of ammonium salts, ammonia and hydrogen are evolved at the cathode; that is, the following hypothetical irreversible reaction occurs:

$$NH_4\,(\text{metal}) \rightarrow NH_3 + \frac{1}{2}H_2.$$

Would metallic ammonium be stable at high pressures? Ramsey[1] was the first to clearly formulate this problem, back in 1951 in a discussion of the internal structure of the planets Uranus and Neptune, which are rich in ammonia and hydrogen.

In 1954, Bernal and Massey[2] attempted to calculate an equation of state for metallic ammonium and to determine the pressure at which a mixture of crystalline ammonia and hydrogen would convert into a metallic phase. Their calculations,[2] based on the Wigner–Seitz approximation, lead to $(60-250)\cdot 10^3$ kg-wt/cm^2 as the pressures at which a crystalline mixture of NH_3 and H_2 would convert into metallic ammonium at $T = 0$ °K.

With progress in high-pressure techniques, an experimental study of this question has been feasible for at least a decade now. The physicists and physical chemists working in the field of high pressures, however, apparently never looked in the geophysical and astronomical literature before the "hydrogen boom," whose beginning can be set at the publication of Ashcroft's paper.[3] For whatever reason, it was only extremely recently[4] that an effort was undertaken to produce metallic ammonium experimentally. It should be noted that even Ramsey was aware that in an attempt to produce metallic ammonium from a mixture of hydrogen and ammonia it would be necessary somehow to prevent the dissociation of molecular hydrogen, since otherwise the original mixture might be in a metastable state at pressures far higher than that required for the equilibrium transition.[1)]

Because of this circumstance and also because of the difficulties in working with gases, Bundy[4] carried out an experimental study of the electrolysis of molten NH_4Cl at a pressure of 80 kbar. The result was negative. It should be emphasized, however, that the electrolysis of molten NaCl under the same conditions does not result in the deposition of Na at the cathode. Bundy concluded that something not understood was occurring in the electrochemical reactions at high pressures and temperatures. Bundy also reported[4] that A. L. Ruoff at Cornell had carried out electrolysis of NH_4I at a pressure of 200 kbar and at temperatures in the range 300–400 °C. Again, the result was negative.

Stevenson recently reported new calculations of the energy and equation of state of metallic ammonium.[5] These calculations were also based on the Wigner–Seitz method, but the procedure used to calculate the ion potential was different from that used by Bernal and Massey.[2]

To estimate the pressure at which a crystalline mixture of ammonia and hydrogen converts into a metal, Stevenson[5] used comparatively recent experimental data on the equation of state of ammonium and hydrogen at high pressures. Accordingly, Stevenson's data[5] seem more plausible than the corresponding estimates of Bernal and Massey.[2]

Stevenson's results[5] can be summarized by saying that the compressibility of a mixture of solid NH_3 and solid H_2 is high enough that this mixture is stable in comparison with the metallic phase at pressures up to at least 1 Mbar. From the experimental standpoint, this problem is thus closely related to the problem of metallic hydrogen and is at least as difficult. Nevertheless, it appears that the properties of metallic ammonium should be extremely unusual, and the whole problem deserves experimental and theoretical study.

[1)] Obviously, this problem also arises in experimental attempts to produce metallic hydrogen.

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