TABLE 1

COMPARISON OF OBSERVED INTERPLANAR *d* SPACINGS WITH THOSE CALCULATED FOR YbO AND A-Yb_2O_3

d(obsd), Å		YbO[a]		A-Yb_2O_3[b]	
Before washing	After washing	*d*(calcd), Å	*hkl*	*d*(calcd), Å	*hkl*
3.17	3.17			3.19	100
2.94	2.94			2.95	002
2.82		2.82	111		
2.79	2.80			2.81	101
2.44		2.44	200		
2.16	2.15			2.16	102
2.10	2.10				
1.91	1.91				
1.82	1.82			1.83	110
1.72		1.72	220		
1.69					
1.67	1.67			1.67	103
1.60	1.60			1.60	200
1.53	1.53			1.53	112
1.47	1.47	1.47	311	1.47	004

[a] $a = 4.87$ Å. [b] $a = 3.68$ Å, $c = 5.59$ Å.

0.02 Å, a value in good agreement with that reported by Rau.[7] There is insufficient evidence to permit positive identification of any other europium–oxygen phase.

The diffraction patterns of the ytterbium–oxygen products contain reflections assignable to the A form of Yb_2O_3 with lattice constants of $a = 3.68 \pm 0.04$ Å, $c = 5.59 \pm 0.04$ Å, and $c/a = 1.52$. The molar volume of 41.7 cm^3 falls on the molar volume *vs.* ionic radius line plotted by Hoekstra.[8] Owing to the diffuseness of the patterns, it is difficult to obtain reliable relative intensities. There is no apparent change in the reflections when this phase is annealed at 110° for several weeks, but after a few days at 230° reflections of both the A and C forms of Yb_2O_3 are present. Even after 1 month at 230° the A form is still present. However, when the sample is heated 1 hr at 850°, the pattern is that of well-annealed C form. We have seen no indication for the reverse transition from the C to the A form.

The diffraction patterns of samples which have neither been washed nor heated contain reflections which probably result from a YbO phase isostructural with EuO. The destruction of this phase upon heating or acid washing, while not allowing us to prove that it is not nitrogen stabilized and hence similar to the Sm–O–N system,[9] is parallel to results obtained for EuO which had been prepared by the reduction of EuOCl with LiH at elevated temperature. From the lattice parameter for this cubic phase ($a = 4.87 \pm 0.01$ Å) and an oxide radius of 1.40 Å obtained from the EuO lattice parameter and an Eu(II) radius of 1.17 Å, the calculated Yb(II) radius is 1.03 Å. Values of the Yb(II) radius calculated from YbSe and YbTe are 1.017 and 1.054 Å, respectively. The three lines in the pattern which are not assigned to YbO or A-Yb_2O_3 do not permit identification of another ytterbium–oxygen phase.

At least five different forms designated A, B, C, H, and X, the latter two observable only when the temperature is greater than 2000°, are recognized for the various lanthanide sesquioxides. The relative stabilities and the reversibility of the transformations among the A (hexagonal), B (monoclinic), and C (cubic) forms are not clearly resolved as has been described in reviews by Brauer[10] and Foex and Traverse.[11] This A-Yb_2O_3 is particularly noteworthy in two respects. First, the A form has not been observed previously for any of the heavy lanthanides, and, second, the A form undergoes a transition to the C form with increasing temperature in contrast with the C to A transitions observed for La_2O_3, Nd_2O_3, Pr_2O_3, and Y_2O_3.[12,13]

The unsuccessful attempts of Brauer, *et al.*,[14] to prepare YbO by LiH reduction of YbOCl or reaction of Yb with Yb_2O_3 are understandable in view of the low temperature required for its preparation. The form of the Yb_2O_3 produced initially by oxidation of YbO could not be determined.

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Metal–Ammonia Solutions. VII. The Electrolysis of Liquid Ammonia Solutions of Aluminum(III) Iodide and Magnesium(II) Chloride

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Liquid ammonia solutions of alkali and alkaline earth metals as well as of tetraalkylammonium radicals can be prepared by the electrolysis of solutions of the corresponding alkali and alkaline earth metal or tetraalkylammonium halides.[1] Spectroscopic results indicate that these solutions are indistinguishable from solutions containing the solvated electron which arise from, for example, the dissolution of sodium or potassium in liquid ammonia. In the course of these investigations an attempt was made to generate liquid ammonia solutions of both aluminum and magnesium by

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[1] (a) R. K. Quinn and J. J. Lagowski, *J. Phys. Chem.*, **72**, 1374 (1968); (b) *ibid.*, in press.

the electrolysis of the corresponding salts. Liquid ammonia solutions of aluminum iodide and magnesium iodide were prepared in an electrolysis apparatus incorporating an optical cell using the techniques previously described.[1] The results of a simple calculation using the optical parameters of the cell (fused silica windows with a 0.421-mm path length), the known extinction coefficient for the solvated electron ($5 \times 10^4\ M^{-1}\ \text{cm}^{-1}$),[2] and the assumption that the spectrometer was sensitive to 0.1 absorbance unit suggested that a concentration of 5×10^{-5} equiv/l. of solvated electrons (1.5×10^{-4} mol/l. of Al or 10^{-4} mol/l. of Mg) could be detected in these experiments.

Electrolysis of ammonia solutions of anhydrous AlI_3 and $MgCl_2$ for extended periods of time gave only a noncondensable gaseous product at the cathode; the solution in the cathode compartment, which was originally clear, became increasingly turbid as electrolysis continued. The gas was identified as hydrogen by mass spectroscopy. The solid products formed in the cathode compartment were isolated by evaporating the solvent, and the residue was evacuated for several hours at room temperature. The residue contained metal ions (either aluminum or magnesium), reacted with water to liberate ammonia (a reaction typical of metal amides), but resisted further characterization. In spite of repeated attempts in which the temperature and the concentration of the metal salt were varied it was not possible to detect the presence of the solvated electron in the cathode compartment spectroscopically during the course of electrolysis of either AlI_3 or $MgCl_2$ solutions.

A previous report on the electrolysis of liquid ammonia solutions of AlI_3 suggested that a solution of electrons could coexist in the presence of a "considerable concentration of aluminum ion";[3] the results of a potentiometric titration of an AlI_3 solution with potassium dissolved in ammonia gave results indicating that Al^{2+} and Al^{+} might be formed in this process.[4] Similar observations have been made from experiments on the anodic dissolution of aluminum in the presence of NO_3^-.[5]

The maximum rate of electrolysis in these experiments, 50–100 times less than that previously reported,[3] was limited by the solubility of the metal halides in liquid ammonia and the small cell constant for the system. Our experiments suggest that solvated electrons cannot coexist with Al^{3+} or Mg^{2+} in liquid ammonia under these conditions because of the ammonolysis of these species to give NH_4^+; the first step in the ammonolysis reaction of Al^{3+} is given in eq 1.

$$Al(NH_3)_x(NH_3)^{3+} + NH_3 \rightleftharpoons Al(NH_3)_{x-1}NH_2^{2+} + NH_4^+ \qquad (1)$$

It is well known that NH_4^+ reacts with solvated electrons to give hydrogen (eq 2). Presumably the partially ammonolyzed metal-containing species can undergo further ammonolysis to give, eventually, a solvated metal amide which is an insoluble[4] or partially ammoniated species (eq 3–5). The apparent success of forming solutions containing solvated electrons and Al^{3+} can be attributed to a difference in the rate at which electrons could be introduced into the solution and the rate at which solvolytic reactions occurred.

$$NH_4^+ + e(NH_3)_x^- \rightleftharpoons (x + 1)NH_3 + 0.5H_2 \qquad (2)$$

$$Al(NH_3)_{x-1}(NH_2)^{2+} + NH_3 \rightleftharpoons Al(NH_3)_{x-2}(NH_2)_2^+ + NH_4^+ \qquad (3)$$

$$Al(NH_3)_{x-2}(NH_2)_2^+ + NH_3 \rightleftharpoons Al(NH_3)_{x-3}(NH_2)_3 + NH_4^+ \qquad (4)$$

$$Al(NH_3)_{x-3}(NH_2)_3 + NH_3 \rightleftharpoons Al(NH_3)_{x-4}(NH_2)_4^- + NH_4^+ \qquad (5)$$

In addition, it might be expected that the acidity of some of the partially ammonolyzed aluminum-containing species, *e.g.*, $Al(NH_3)_{x-2}(NH_2)_2^+$, would be negligibly small with respect to the solvent so that a reaction with solvated electrons would not occur. Thus, the number of equivalents of electrons consumed in the attempted electrolysis of either AlI_3 or MgI_2 solutions would depend upon the acidity of the intermediate metal-containing species that are related by consecutive equilibria as well as by their relative solubilities.

The solubility of a metal in liquid ammonia depends on its ionization energy,[6] but the compatibility of the solvated electron with cationic species appears to be related to the ease of ammonolysis of the latter. As is the case in aqueous solutions[7] it might be expected that the extent of solvolysis reactions would be related to the charge density of the cation. The charge densities[8] of the cationic species present in the stable metal–ammonia solutions formed by the alkali (Li, Na, K, Cs) and alkaline earth metals (Ca, Sr, Ba) are in the range 1.09–0.05 $e^-/\text{Å}^3$. Solutions of europium and ytterbium, which dissolve to form the divalent ions,[9] contain cations with charge densities of 0.24 and 0.40 $e^-/\text{Å}^3$, respectively. In contrast to these values, the charge densities of Mg^{2+} and Al^{3+} are 1.74 and 7.86 $e^-/\text{Å}^3$, respectively; the former value is 60% greater than the charge density of Li^+ (1.09 $e^-/\text{Å}^3$) which forms stable metal–ammonia solutions.

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