reagents were mixed and allowed to react at room temperature for specified lengths of time, usually 1–10 min. The presence of isocyanide is indicated by a white to blue color change in the detector tube.[11] The yields of isocyanide can be semiquantitatively estimated from the intensity of the color. The lowest amount of methyl isocyanide detectable is approximately 0.1 μg.

Analyses.—All elemental analyses were performed by the Analytical Research Department, Chemical Research Laboratory, Edgewood Arsenal, Md.

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The Preparation of Rare Rarth Nitrides from Amalgams

BY B. MAGYAR

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Many transition and rare earth metal compounds have been examined as new ferromagnetic semiconductors, but this important property has so far been demonstrated conclusively only in some compounds of europium(II)[1,2] and chromium(III).[3,4] Investigations of the rare earth nitrides have not been definitive, since the samples which have been prepared either by direct combination of the elements[5–7] or by reaction of the hydride and nitrogen[8] have contained amounts of nitrogen to metal in less than the stoichiometric ratio. The samples contained either unreacted metal or a second anion, presumably O^{2-}. If air is carefully excluded during preparation of the nitride, any oxygen present must have preexisted in the metal as an impurity. Such oxygen can probably not be removed by outgassing the metal, since, at the elevated temperatures required for outgassing, oxygen is chemically bound by the metal. Since the oxygen content of commercially available metals is in the range 0.1–1.0 mol %, products with a nitrogen/metal ratio of 0.99 are to be expected. Lower ratios than this must be attributed to incomplete reaction of the metal with nitrogen. The incomplete reaction of the metal with nitrogen presumably occurs for kinetic reasons. During the reaction the metal particles become coated with nitride, and the diffusion of both metal and nitrogen through this layer appears to be slow. In order to complete the reaction, the nitridation would have to be continued for an impracticably long period. This problem might be overcome by continuous pulverization during the reaction or by carrying out the reaction with the metal in the gaseous, molten, or dissolved state. From the kinetic standpoint, combination of the molten metal with nitrogen, atomized in an electric arc, would perhaps be the best method.[9] Some nitrides of the transition metals have already been obtained by treatment of liquid amalgams with ammonia,[10] but the products were obtained in highly disperse state and were not easily separable from the large amounts of mercury present. For preparative purposes, it is preferable to use solid amalgams having a higher content of rare earth. The solubility[11] of the rare earth metals in mercury is very small. "Amalgams" with a higher rare earth content are suspensions of different solid intermetallic compounds in mercury. These compounds are of the type LnHg_x, where $x = 1$–4, and have a moderate thermal stability.[12] Their decomposition temperatures are well below the melting points of the rare earth metals. Therefore, the thermal decomposition of the amalgams yields solid rare earths in a highly dispersed form, thus offering good conditions for direct union with nitrogen. The following scheme was found to yield stoichiometric rare earth nitrides

$$\mathrm{LnHg}_x(\mathrm{s}) + 0\cdot 5\mathrm{N}_2(\mathrm{g}) \xrightarrow{500-1000^\circ} \mathrm{LnN}(\mathrm{s}) + \mathrm{Hg}(\mathrm{g})$$

where $x = 1$–4 and Ln = La, Pr, Nd, Gd, or Tm. Table I contains the stoichiometric ratio and the lattice constants of some nitrides obtained by the amalgam method. The composition of the amalgam seemed to have no influence upon the composition of the obtained nitride. There appeared to be little advantage in using a nitrogen–ammonia mixture for the nitridation as the reaction with nitrogen alone was sufficiently rapid. This method readily afforded mixed crystals of rare earth nitrides at a relatively low temperature. This represents a considerable advantage over the more usual method of heating the two nitrides together, requiring a high temperature, presumably owing to slow diffusion in the nitride phase. The systems $\mathrm{Gd}_{1-x}\mathrm{Pr}_x\mathrm{N}$ and $\mathrm{Gd}_{1-x}\mathrm{La}_x\mathrm{N}$ were studied. The mutual solubility of the nitrides was readily estimated from a plot of the unit cell dimensions against the chemical composition (see Figure 1). At 1000°, the PrN-rich phase dissolved 46 mol % of GdN, whereas the GdN-rich phase dissolved up to 7 mol % of PrN only. Upon nitridation, mixed amalgams of the composition $\mathrm{Pr}_{1-x}\mathrm{Gd}_x\mathrm{Hg}_y$ yielded two phases, both having the NaCl structure, when x had a value between 0.07 and 0.54. The $\mathrm{Gd}_{1-x}\mathrm{La}_x\mathrm{N}$ system behaved similarly, where the solubility gap extended from $x = 0.00$ to $x = 0.60$.

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(1) B. T. Mattias, R. M. Bozarth, and J. H. Van Vleck, *Phys. Rev. Letters*, **7**, 160 (1961).

(2) G. Busch, P. Junod, M. Risi, and O. Vogt, Proceedings of the International Confernence on Semiconductors, Exetter, 1962, p 729.

(3) P. K. Baltzer, H. W. Lehmann, and M. Robbins, *Phys. Rev. Letters*, **15**, 493 (1965).

(4) I. Tsubokawa, *J. Phys. Soc. Japan*, **15**, 1664 (1960).

(5) H. A. Eick, N. C. Baenziger, and L. Eyring, *J. Am. Chem. Soc.*, **78**, 5987 (1956).

(6) A. Iandelli, *Z. Anorg. Allgem. Chem.*, **288**, 85 (1956).

(7) G. Busch, P. Junod, F. Levy, and O. Vogt, Proceedings of the International Conference on Magnetism, Nottingham, England, 1964, p 472.

(8) D. E. La Valle, *J. Inorg. Nucl. Chem.*, **24**, 930 (1962).

(9) R. J. Gambino and J. J. Cuomo, *J. Electrochem. Soc.*, **113** (4), 40 (1966).

(10) P. Ettmayer, Thesis, Vienna, 1964.

(11) A. F. Messing and O. C. Dean, ORNL-2871, Oak Ridge National Laboratory, Oak Ridge, Tenn., June 1960.

(12) W. Lugscheider, Thesis, Vienna, 1964.

TABLE I

	PrN	NdN	GdN	TmN
Method of prepn of $LnHg_x$	A	A	B	B
x	1.26	2.09	20.0	10.0
N/Ln (±0.005)	0.995	0.970	0.998	0.990
a_0 (±0.001), Å	5.169	5.131	4.985	4.813

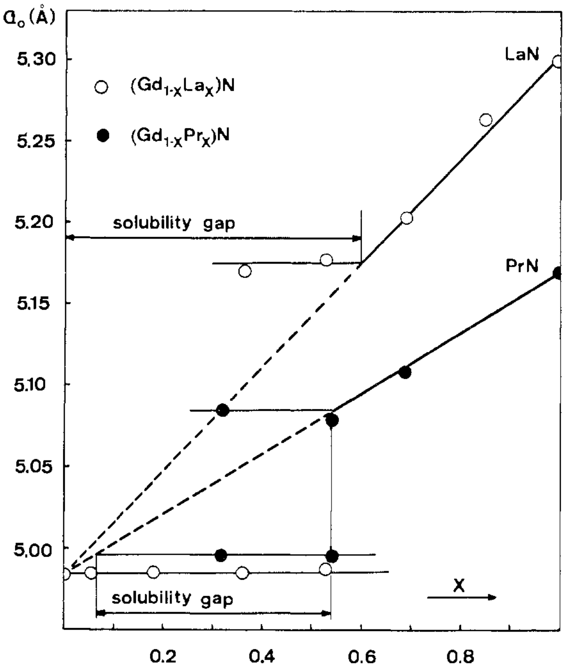

Figure 1.—Mutual solubility in the systems $Gd_{1-x}La_xN$ and $Gd_{1-x}Pr_xN$ at 1000°.

Experimental Section

All manipulations were carried out under nitrogen or argon.

(1) **Preparation of Amalgams. Method A.**—The dehydrated chloride was dissolved in methanol and electrolyzed with a graphite anode and a mercury cathode.[13] Electrolysis was carried out in a vessel provided with ground-glass joints to permit introduction of a graphite anode (diameter 12 mm), a stirrer, a combined inlet and outlet for nitrogen, a water jacket, and a tap on the bottom. A voltage of about 40 V was required to maintain a current of 1–2 A, depending upon the distance between the anode and cathode (10–20 mm), the concentration of the rare earth chloride (half-saturated), and the temperature (about 20°).

Owing to the large surface area of the cathode, a total current of 1 A corresponded to a density of 0.04 A/cm². The electrolysis was stopped after 20–40 hr, and the amalgam obtained was run off into a two-bulb vessel. Any electrolyte carried with the amalgam was washed out with methanol under nitrogen. This vessel was then evacuated and sealed. The excess of mercury was then distilled from bulb 1 into bulb 2 and finally the vessel was sealed between the two bulbs. The composition of the amalgam obtained in bulb 1 depended upon the temperature at which the mercury was distilled (200–300°).

Method B.—The amalgams of the rare earths were obtained by heating the metal (or metals for mixed nitrides) at 300–350° in a sealed glass tube with 20–30 times its weight of mercury. This at the same time achieved some purification of the metal, since the oxidation products were lighter than mercury and separated out at the surface of the amalgam. The amalgam was obtained as a thick pulpy solid and could be nitrided directly.

(2) **Nitridation.**—For the preparation of the nitride, the amalgam was placed in two molybdenum boats. The first of these, containing about one-fifth of the total amalgam, was used for further purification of the nitrogen, since the rare earth nitride formed from the amalgam was a very good absorbent for traces of oxygen. The boats were placed in a silica tube and heated in a stream of purified nitrogen in steps, as follows: 2–3 hr at 340°, 2–3 hr at 500°, 12–15 hr at 700°, and 1–5 hr at 1000°. The formation of the nitride is complete at 700°, but the final heating period is necessary to increase the particle size sufficiently in order to obtain sharp reflections in the X-ray powder diagrams. The use of rubber and plastic tubing for the nitrogen line was avoided because of their permeability to moisture. All connections were made from glass tubes, with spherical joints included at suitable positions to maintain flexibility.

(3) **Analyses.**—Analyses for the rare earths and nitrogen were carried out by complexometric and Kjeldahl assays, respectively, after dissolution of the nitride in 1 *M* hydrochloric acid. Owing to the violence of the reaction, especially with nitrides not annealed at high temperatures (1200°), the rate of dissolution in acid had to be carefully controlled to prevent loss of ammonia. This was conveniently accomplished by sealing a weighed amount of nitride in a glass bulb, fitted with a side arm drawn out into a capillary. For digestion, the capillary was broken, and when the dark nitride had become light in color owing to conversion into $LnCl_3 \cdot xH_2O$ and $Ln(OH)_3 \cdot xH_2O$, the bulb was broken completely, and the flask was closed until dissolution was complete.

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[13] H. S. Booth, *Inorg. Syn.*, **1**, 15 (1939).

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Chlorovinylation of Palladium

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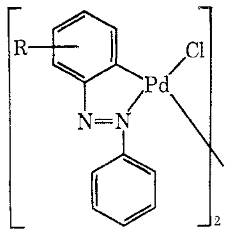
Recently some organopalladium compounds from the reactions of palladium(II) salts with unsaturated organics have been investigated by several workers.[1–5] For example, Anderson and Burreson have prepared acetoxy palladium(II) olefin adducts.[1] Cope and coworkers have found palladium(II) halides to react with azobenzenes to give I[2] and with allylic amines to give II.[3]



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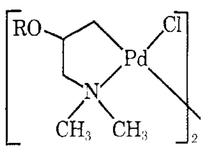

II

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(1) C. B. Anderson and B. J. Burreson, *J. Organometal. Chem.* (Amsterdam), **7**, 181 (1967).

(2) A. C. Cope and R. W. Siekman, *J. Am. Chem. Soc.*, **87**, 3272 (1965).

(3) A. C. Cope, J. M. Klieman, and E. C. Friedrich, *ibid.*, **89**, 287 (1967).

(4) J. Tsuji and H. Takahashi, *ibid.*, **87**, 3275 (1965).

(5) J. K. Stille and R. A. Morgan, *ibid.*, **88**, 5135 (1966).