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FINAL REPORT

A STUDY OF THE STRUCTURE OF THE TRANSITION METAL HYDRYLS

A Research Project Supported by NASA Grant
in the Space-Related Sciences

NsG-518

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Submitted by
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I. ABSTRACT

The purpose of this program was to use the various techniques available in the Chemistry and Chemical Engineering Division and the Metallurgy Division of the Denver Research Institite to determine the crystal and molecular structures of the transition metal hydryls, principally the rhodium hydryls of formulae: $(LiH)_4$ Rh and $(LiH)_4$ RhH.

Many attempts were made to observe the infrared absorption spectra of these and other hydryl compounds using the mull technique. Although broad bands were observed for all compounds studied, the results were not reproducible and failed to show expected shifts when deuterium was substituted for hydrogen. An evaporation technique was developed for obtaining thin films of materials on KBr plates for infrared analysis. This technique proved to be very successful for LiH and LiD, but, when applied to the hydryls, decomposition took place during evaporation and the films were not representative of the original compounds. All attempts to find a solvent for the hydryls were unsuccessful. It might be concluded that the observed broad absorption bands indicate predominantly ionic bonding in these materials, but any conclusions should await the development of a technique for observing the true infrared absorption spectra of these compounds.

Single crystal X-ray diffraction analysis has resulted in the unambiguous determination of the unit cell type and size of $(LiH)_4$ Rh. The cell is body centered tetragonal with $a_0 = b_0 = 6.36A^\circ$ and $C_0 = 4.09A^\circ$. The volume of this cell is 1.65×10^{-22} cc, and the theoretical density, based on two $(LiH)_4$ Rh molecules per cell, is 2.71 gms per cc. Some recently measured density values are 3.05 and 3.25 gms per cc. Although X-ray diffraction analysis cannot determine the positions of the hydrogen and lithium atoms in the unit cell, knowing the type and dimensions of the cell permits speculation of logically possible atom arrangements. One such arrangement would be a squashed tetrahedron with rhodium in the center and LiH groups extending out from the rhodium. This and other possible arrangements will be checked in future work using NMR spectra analysis and neutron diffraction analysis.

II. INTRODUCTION

A few years ago J. D. Farr* of the Los Alamos Scientific Laboratory discovered a new group of compounds which he called the hydryls. Specifically, he reacted lithium hydride (LiH) with rhodium (Rh) and obtained a compound of simplest formula $(LiH)_4Rh$. He found that this compound would take on additional hydrogen until a compound of simplest formula $(LiH)_4RhH$ was obtained. There is a direct analogy between the apparent stoichiometries of these compounds and those of the rhodium carbonyls. The latter compounds have the formulae: $Rh_2(CO)_8$ and $Rh(CO)_4H$. It was this analogy that led Farr to term the new compounds "hydryls."

The apparent analogy between the hydryls and the carbonyls coupled with the fact that there are fifteen transition metals which form carbonyls, suggested to this writer (Magee) that there may be many hydryl compounds besides those of rhodium. Such compounds are of interest for two main reasons: in the first place the chemical bonding exhibited by the hydryls is unique and achieving an understanding of this type of bonding is of fundamental importance; and, secondly, the high hydrogen content of the hydryls and the fact that these compounds contain both low and high atomic number atoms makes them of potential interest for nuclear reactor materials applications. Interest in these materials led to a two year research program sponsored by the Joint U. S. -EURATOM Research and Development Board to study the hydryls of the cobalt metals: cobalt, rhodium, and iridium. It is not pertinent here to describe the results of this study in detail; suffice it to say that the hydryls of iridium were prepared** along with those of rhodium, and the stabilities and thermodynamic properties of these compounds were determined using equilibrium hydrogen pressure measurements as a function of temperature and composition as the basic tool. Throughout this work X-ray diffraction patterns made by the powder technique were used for identification purposes. These powder patterns could be analyzed in the cases of the binary intermediate phases LiRh and LiIr to give crystal structures. The patterns for the hydryls themselves, however, could not be analyzed unambiguously. Thus, at the conclusion of the program sponsored by the U. S. -EURATOM Research

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* Farr, J. D., J. Inorg. Nucl. Chem., <u>14</u>, 202-207, (1960).

** Evidence was found also for the existence of a cobalt hydryl. However, a reproducible method of synthesis could not be found.

and Development Board, much had been learned about the chemical and thermodynamic properties of the hydryls, but their crystal structures were still undetermined.

It was the intent in the work described in this report to concentrate on the determination of the structure of the hydryls. It was intended to use, in addition to X-ray diffraction, other available techniques for structural determinations. Two such techniques are infrared absorption spectra analysis and nuclear magnetic resonance band analysis. If the hydryls are composed of discrete molecules with at least partially covalent bonds between, for example, hydrogen and rhodium or iridium, then the characteristic vibrations of the molecule would be observable in the infrared absorption spectrum of the compound. An analysis of the observed characteristic frequencies of the molecule gives information about its symmetry and, hence, about the arrangement of the atoms in the molecule. If, on the other hand, the bonding in the crystalline solid is ionic, then the spectrum would show a broad absorption band, rather than a number of discrete narrow bands, corresponding to the optical branch of the lattice vibration distribution.

In the crystalline solid, regardless of whether or not discrete molecules are present, the hydrogen atoms in the hydryls are located in specific locations in the lattice. The particular arrangement of the hydrogen atoms would be reflected in the shape of the proton magnetic resonance band of the crystalline material. Although this is a well-established technique and many compounds have been studied using it, analysis of proton magnetic resonance band shapes is by no means a simple matter, and complete crystal structures cannot be determined using this technique by itself. If, however, a particular arrangement of the hydrogen atoms can be assumed, the general shape of the PMR band can be predicted. The predicted shape can then be compared with the experimentally observed shape to check the validity of the assumed hydrogen atom positions. It was the intent in this study to use X-ray diffraction to determine the unit cell type and size* of the hydryls, then to assume different hydrogen arrangements and check them against the proton magnetic resonance band shape.

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* Because of the low X-ray scattering power of lithium and hydrogen, their positions in the unit cell cannot be determined by means of X-ray diffraction.

The following sections of this report will describe the results obtained in this research program in these various approaches to the determination of the structure of the hydryls. A great deal more work remains to be done before these compounds are thoroughly understood. A proposal for a three-year research program of broad range has been submitted to the National Science Foundation for continuation of this work. The work described here, while as yet incomplete, has brought to light many interesting observations and will form the basis upon which future work on these compounds will proceed.

III. PREPARATION OF MATERIALS

The starting materials, lithium and lithium hydride, and the hydryls themselves are very reactive with air and moisture. Consequently, all handling of these materials had to be done in an inert atmosphere box. Purified helium was used for the inert atmosphere. All materials preparation was carried out in one or another Sieverts apparatus, a vacuum system suitable for adding known amounts of a gas to a condensed phase at relatively high temperature. A typical Sieverts apparatus is shown in the photograph in Figure I. At the extreme left is seen the purification system for hydrogen gas. Next to the right is the burette for measuring the amount of gas added to the system. In the center is seen a furnace with the reaction tube suspended in it. The reaction tubes used were made of quartz or alumina. To the far right is seen the manometer for measuring the pressure of the gas in the system. Not shown are the pressure gauges, the oil diffusion pump, and the forepump.

A. Preparation of Lithium Hydride

Lithium hydride is prepared as follows: Lithium metal is loaded into a high-purity iron crucible* in the inert atmosphere box. With a rubber stopper in place the crucible is transferred to the reaction tube of the Sieverts apparatus as quickly as possible. The rubber stopper is removed and the system pumped down to the highest vacuum attainable (about 10^{-6} mm of Hg not including the pressure of Hg vapor). The reaction tube is heated to about 200° C and a batch of hydrogen gas is added. The temperature is raised to about 700° C (above the melting point of LiH), at which temperature the reaction takes place quite rapidly. More hydrogen gas is added as needed until reaction ceases (pressure remains constant). The temperature is lowered to room temperature, the excess hydrogen gas pumped out, and the system opened to argon gas. The crucible is again stoppered and is transferred back to the inert atmosphere box. The LiH is chipped out of the crucible and a powder sample prepared for X-ray diffraction analysis.

Despite precautions against contamination it is difficult to obtain a batch of LiH, the X-ray pattern of which does not show the presence

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* The high purity iron used for these crucibles was obtained from the Westinghouse Electric Corporation. It is sold under the trade name, "puron."

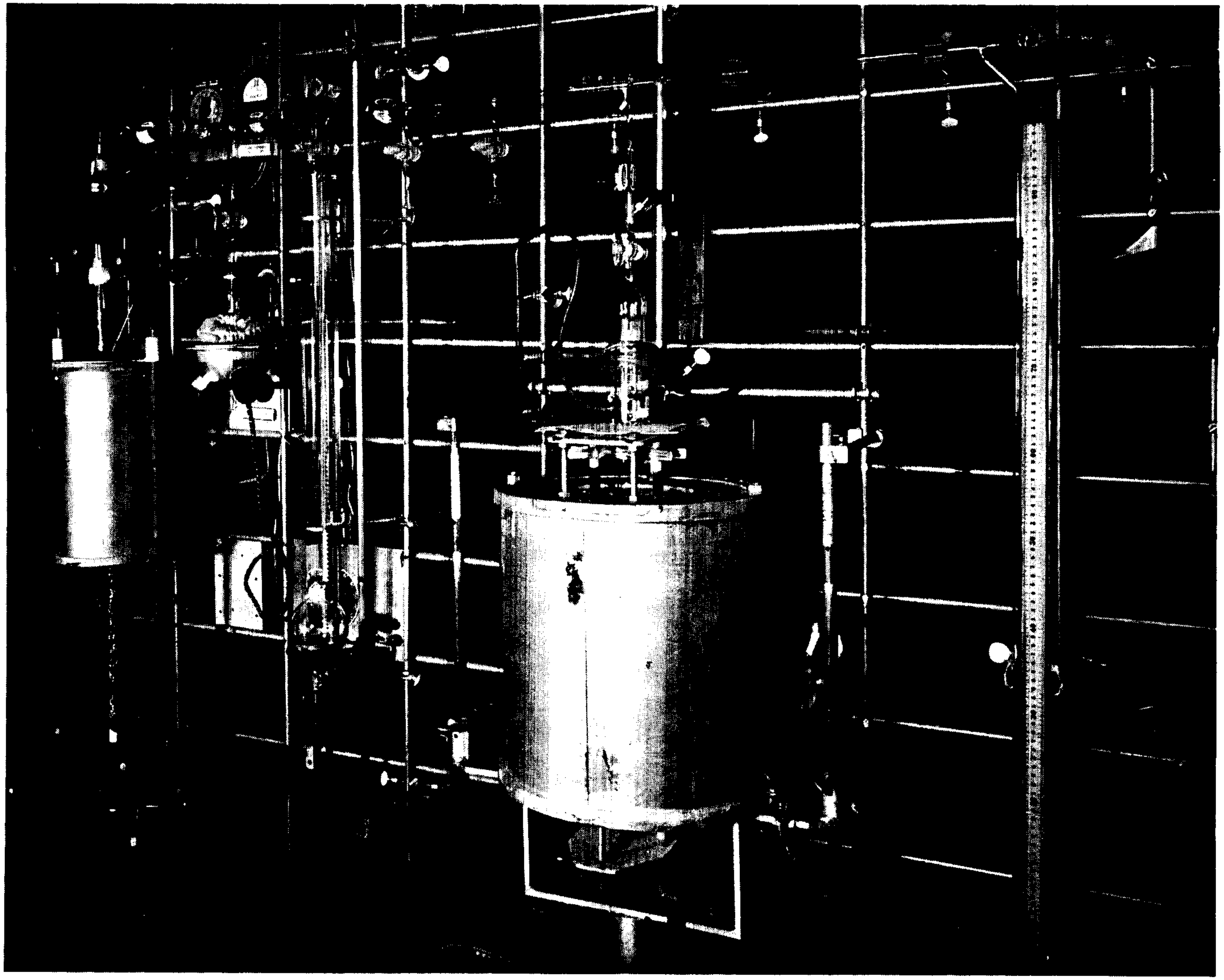

Figure I. Photograph of Sieverts Apparatus of lithium carbonate, lithium hydroxide, lithium oxide, lithium nitride, or any combination of these. When a relatively pure batch is prepared, it is used in the synthesis of the hydryls as described below. Lithium deuteride is prepared in the same manner as is lithium hydride using deuterium gas in place of hydrogen gas.

B. Preparation of the Hydryls

The hydryls can be prepared in two ways: A four to one molar ratio mixture of lithium and rhodium or iridium can be reacted with hydrogen gas at temperatures of the order of 700° C; or a four to one molar ratio mixture of LiH and Rh or Ir can be heated to the same temperature range under vacuum. In the former method, unless the amount of hydrogen gas added is controlled, the final product is $(LiH)_4RhH$ or $(LiH)_4IrH$. In the latter method the products are $(LiH)_4Rh$ or $(LiH)_4Ir$. These compounds can then be reacted with hydrogen to form the compounds with an additional atom of hydrogen. The latter method was used in this work.

The procedure for preparing the hydryls is as follows: A 4 to 1 molar ratio mixture of LiH (or LiD) and Rh (or Ir) powders are loaded into a high purity iron crucible in the inert atmosphere box. The crucible is transferred to the reaction tube of the Sieverts apparatus and the system is pumped down. In preparing the rhodium compound the reaction tube is heated to about 650° C. This temperature is above the melting point of $(LiH)_4Rh$ (585° C) and the reaction proceeds quite rapidly. After holding at this temperature for one half hour or so, the temperature is reduced very slowly through the freezing point of the compound. This is done in an attempt to form large crystals of the solid material. There is a hydrogen pressure buildup in the systems when the temperature is raised. As the temperature is lowered after the reaction takes place, the hydrogen pressure decreases. At the melting point this pressure is about 20 mm of Hg. At room temperature the hydrogen pressure is too low to measure on a manometer.

In the preparation of the iridium compound the temperature is raised to over 700° C, that is, above the melting point of LiH. The iridium hydryl itself is solid at this temperature,* and the reaction is slower than that between rhodium and LiH. The holding time at temperature is therefore longer in this case. Again the hydrogen pressure decreases as the temperature is lowered to room temperature.

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* The temperature has been raised to 800° C without observing melting of $(LiH)_4Ir$.

When the reaction tube is at room temperature the crucible is transferred to the inert atmosphere box and some of the $(LiH)_4Rh$ or $(LiH)_4Ir$ chipped out. The crucible containing the rest of the compound is returned to the reaction tube. The temperature is raised to 600 or 700°C and hydrogen at about atmospheric pressure is added to the system to form $(LiH)_4RhH$ or $(LiH)_4IrH$. The hydrogen pressure decreases until the reaction is completed. The temperature is lowered to room temperature, the excess hydrogen pumped out, and the crucibles transferred to the inert atmosphere box. Powder samples of each material are prepared for X-ray diffraction analysis.

The procedures described above were used in this program for the preparation of the following compounds: $(LiH)_4Rh$, $(LiH)_4RhH$, $(LiD)_4Rh$, $(LiD)_4RhD$, $(LiH)_4Ir$, and $(LiH)_4IrH$.

IV. INFRARED ABSORPTION SPECTRA ANALYSIS

The infrared absorption spectra of LiH, LiD, and all of the hydryl compounds mentioned in the previous section were determined in the 2 to 30 micron region. A Beckman Infracord Spectrophotometer with NaCl optics was used in the 2 to 15 micron region, and a Beckman IR-7 Spectrophotometer with KBr optics was used in the 15 to 30 micron region.

First attempts at obtaining absorption spectra made use of the well-known mull technique for solid materials. In this technique the solid material is ground to small particle size in an oil such as Nujol. The resulting mull is then spread thinly on KBr, NaCl, or polyethylene plates (depending on the region of the spectra to be observed) for spectral analysis. The results obtained using this technique were not encouraging. Although absorption bands were observed for all the materials studied, these bands could not be interpreted with any degree of confidence. In the first place, spectra obtained from different mulls of the same material were not reproducible. Secondly the spectra obtained from all the materials (regardless of whether or not they contained hydrogen or deuterium) were of the same general shape with a broad absorption band in the 20 micron region. While the single broad band might indicate ionic bonding in all these materials, the lack of specificity of the absorption bands and the failure to observe shifting when deuterium replaced hydrogen in the compounds led us to believe that the mull technique was not giving a real indication of the absorption properties of these materials. This belief was confirmed by the fact that the spectra obtained for LiH and LiD did not correspond to the spectra for these materials reported by Zimmerman and Montgomery.*

The difficulty with the mull technique, it was felt, was that the particle size was not small enough to observe the true absorption spectra. For ionic compounds the appearance of the absorption peak is very much a function of the sample thickness. For such compounds very thin films (less than about 2 microns thick) must be employed if the true shape of the band is to be determined. Consequently much effort was expended in developing a technique of depositing thin films of the materials of interest in this study.

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* Zimmerman, W. B., and Montgomery, D. J., Physical Reviews, 120, 405, (1960).

The first materials studied were LiH and LiD which are known to be ionic compounds and therefore have single broad absorption bands. In addition, the ratio of the wavelength of the absorption peak of LiD to the wavelength of the absorption peak of LiH should be equal to the square root of the ratio of their reduced masses. This latter ratio is 1.33. Thus, if the observed ratio of wavelength is in agreement with this number, one is assured that the observed spectra are really representative of these materials.

Small samples of LiH or LiD were flash evaporated under vacuum onto KBr or polyethylene plates. The heater used was made of tantalum sheet and could be resistance heated to white heat in a matter of seconds. The KBr or polyethylene plates were positioned at different distances from the heater to obtain different film thicknesses of the evaporated material. After many trials, films with optimum thickness were obtained and very clean cut spectra were observed. The absorption peak for LiH was observed at 17.0 microns and that for LiD at 22.5 microns. The ratio of the latter wavelength to the former is 1.325 in excellent agreement with the predicted value of 1.33. The observed spectra also are in agreement with those reported by Zimmerman and Montgomery.

The excellent results obtained for LiH and LiD led us to attempt using the same evaporating technique for the rhodium hydryls. Thin films were obtained by evaporation of $(LiH)_4Rh$ and $(LiD)_4Rh$. These films showed infrared absorption bands: a single peak at 23.2 microns for $(LiH)_4Rh$ and double peaks at 22.8 and 24.0 microns for $(LiD)_4Rh$. However, these absorption bands cannot be attributed to the hydryl compounds. In one experiment the film obtained by evaporation of $(LiH)_4Rh$ was analyzed for rhodium by means of X-ray fluorescence; no rhodium was found in the film. The tantalum heater from which the material was evaporated likewise was analyzed and was found to contain rhodium. Thus it must be concluded that these materials decompose during evaporation.

It might be expected that $(LiH)_4Rh$ would decompose to form LiH and Rh, and that the film obtained would consist of LiH. That this is not the case, however, is demonstrated by the fact that the film obtained from $(LiH)_4Rh$ absorbs at 22.3 microns rather than at 17.0 microns, the absorption band for LiH. What probably happened was that the hydryl decomposed to Li, H_2 and Rh, and that the initial film formed consisted of lithium. The extremely reactive lithium film then reacted with the constituents of air, despite attempts to prevent exposure to air, to form the oxide, hydroxide, and/or the carbonate.

The observed band at 23.2 microns then must be attributed to one or more of these salts. This conclusion is based on an experiment in which lithium metal was evaporated onto a KBr plate and the absorption spectrum observed. Lithium by itself should show no absorption band in the infrared because it has no permanent dipole moment. However, the film showed an absorption band at 23.2 microns just as did the film from evaporated $(LiH)_4Rh$.

As a result of the work described above, it was obvious that the flash evaporation technique was not suitable for obtaining thin films of the hydryls. Another approach to obtaining infrared spectra was attempted. If the hydryls could be gotten into solution, then either the solution itself could be used to obtain spectra or thin films could be obtained by evaporation of the solvent. The following non-aqueous solvents were tried with $(LiH)_4Rh$: ethanol, diethyl ether, trichloroethylene, acetone, methyl alcohol, benzene, hexane, diethyl formamide, and carbon disulfide. Carbolic acid (phenol in water) was also tried. None of these solvents readily dissolved the hydryl. In the case of ethanol there was evidence of slight dissolution or reaction, but the infrared spectrum showed no bands other than those of ethanol. With diethyl ether the liquid slowly turned yellow indicating, probably, that a reaction was taking place. With carbolic acid the liquid slowly turned red, again indicating reaction. Although the possibilities were not completely exhausted, it appeared that the hydryls were going to resist going into any kind of solution.

No definitive conclusions can be drawn based on the observed infrared absorption spectra of the hydryls. The fact that single broad bands were observed using the mull technique might lead to the conclusion that the bonding in the hydryls is predominantly ionic. However, as stated above, the lack of reproducibility and specificity of the bands makes any conclusions based on them open to grave suspicion. It is felt that perhaps the best approach to obtaining the infrared spectra of the hydryls in future work will be to observe the spectra of these materials in the liquid state. This will require an infrared cell that will operate at 600°C with windows that do not react with the hydryls. Such a cell is not outside the realm of possibility and will be given serious consideration.

V. X-RAY DIFFRACTION ANALYSIS

Before this program started and throughout its course many attempts were made to index the X-ray diffraction pattern of powdered $(LiH)_4Rh$. Some success was achieved in that a possible unit cell was determined from a computer program that fits the observed interplaner distances to a possible crystal structure. The difficulty was that the observed pattern was very complex with many lines, and one is never sure that some or many of the lines are not due to impurities.

Some very significant results have been obtained during the last few months of this program. A Ph. D. candidate in the Department of Metallurgy, Mr. Lynn Lundberg, has been awarded an AEC-ARMU Fellowship to carry out his thesis research at the Los Alamos Scientific Laboratory. His thesis problem is to determine unambiguously the positions of all the atoms in the $(LiH)_4Rh$ lattice. He will use neutron diffraction to determine the positions of the lithium and hydrogen atoms. When he moved to Los Alamos this past summer he took with him a sample of $(LiH)_4Rh$. Looking at this powdered sample under a microscope he was able to pick out a small single crystal of the compound. He mounted the crystal in a precession X-ray camera that was available to him at Los Alamos (our X-ray laboratory does not have this particular kind of camera). With relatively little difficulty he was able to align the crystal along one of its principle axes, and then along its other two axes. Analysis of the resulting X-ray diffraction patterns showed the unit cell to be face centered tetragonal with $a_0 = b_0 = 8.98\text{A}^\circ$ and $c_0 = 4.09\text{A}^\circ$. This is equivalent to a body centered tetragonal cell with $a_0 = b_0 = 6.36\text{A}^\circ$ and $c_0 = 4.09\text{A}^\circ$. The volume of this latter cell is 1.65×10^{-22}cc. Assuming two molecules of $(LiH)_4Rh$ per unit cell, the theoretical density is 2.71 gms/cc. Recent values of the measured density of the material are 3.25 and 3.05 gm/cc. The agreement with the theoretical density is not as good as one would hope, but the material used in the measurements of the density was not homogeneous. The density will be remeasured using a better sample of the hydryl.

The determination of the unit cell type and size is a very significant achievement in this study. It is possible using the known lattice parameters to calculate the lines that should appear on a powder pattern of the material. This has been done, and in comparing the calculated pattern with the observed pattern it is found that many extraneous lines are present in the observed pattern. It is because of these extraneous lines that the powder patterns have not been unambiguously indexed heretofore. The source of these extraneous lines is as yet unknown.

Also, with knowledge of the unit cell dimensions, it is possible to make some assumptions regarding the positions of the hydrogen and lithium atoms in the cell. Assume for example, that a rhodium atom occupies the body centered position. If the LiH groups were arranged tetrahedrally around the rhodium atom the cell would be body centered cubic rather than body centered tetragonal. Since the c_0 value is about two-thirds the value of a_0 or b_0 the angles are obviously not tetrahedral. However, one possibility would be for the molecule to be a squashed tetrahedron. If the tetrahedron were completely squashed the molecule would become planer with the angles between adjacent LiH groups all 90°, and the angles between opposite groups 180°. But if only partially squashed, some of the angles would be greater than tetrahedral and less than 180° and others would be less than tetrahedral but greater than 90°.

This kind of assumed structure can be checked for compatability against the shape of the proton magnetic resonance spectrum. Unfortunately, knowledge of the unit cell type and size of $(LiH)_4Rh$ came late in this program when there were insufficient funds remaining to carry out the NMR work. Also, we have not had a sufficiently pure sample of the hydryl in quantity required for NMR analysis. Using a sample which was not single phase would practically preclude any meaningful analysis. Now that it is known which lines in the powder patterns of the rhodium hydryl represent impurities, steps can be taken to identify and eliminate these impurities.

This work has produced significant information regarding the structure of the hydryls. The work is far from complete and, as stated in the introduction, a proposal for a three year grant has been submitted for continuation and expansion of this work. In future work NMR will be utilized, and this, coupled with the neutron diffraction work at Los Alamos, should completely determine the arrangement of the atoms in the crystalline hydryls.