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Electrical resistivities and magnetic susceptibilities of some rare earth metal-metal halide systems

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ELECTRICAL RESISTIVITIES AND MAGNETIC SUSCEPTIBILITIES

OF SOME RARE EARTH METAL-METAL HALIDE SYSTEMS

by

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In Charge of Major Work

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Iowa State University
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DEDICATION

To my wife

Shirley

whose quiet encouragement

made this possible

INTRODUCTION

One of the more interesting phenomena that has perplexed the inorganic chemist is the solubility of metals in their respective molten halide salts. Although examples were known at the beginning of this century, much of the data has been collected in recent years. As of the present time, the many metal-metal halide systems that have been investigated include those of the alkali and alkaline earth metals plus various transition and post-transition elements. More recently, studies were made on systems involving the lighter lanthanide metals. The phase diagrams of those systems in which there is significant metal solubility have generally been determined in fair detail. The depth of the examination of others varies widely, ranging down to a single measurement.

It is an axiom of the scientific literature that an accumulated mass of experimental data stimulates the publication of review articles. Three have appeared recently. That by Ukshe and Bukun (1) is a short general discussion of these solutions. In their book on fused salts, Delimarskii and Markov (2) devote a chapter to metal-salt systems with their primary concern being the chemical equilibria between alloys and mixed salts. A more comprehensive analysis of metal-salt solutions has been written by Corbett (3) with considerable comment on proposed solute species.

Initially there had been some doubt that the metal truly

dissolved in the molten salt. Lorenz (4, 5) had postulated
that the metal was merely a colloidal dispersion in the molten
salt, but later experimental evidence has discredited this
theory. Although there is general agreement that dissolution
does occur, the nature of the solute species is still the
subject of much dispute. A comprehensive explanation has
yet to be devised and hence each particular system must be
discussed on the basis of its own characteristics.

Three distinct concepts of the nature of the solute spe-
cies are prevalent in the current literature. In the first,
whose chief advocate can be considered to be Cubicciotti, the
melt is assumed to be a pseudo-lattice of halide anions with
the cations occupying an appropriate number of octahedral
holes. On dissolution of the metal in the salt, the metal
atoms enter into the remaining holes. A result of this
theory is that metal solubility should increase with increas-
ing cationic charge since more vacant octahedral sites become
available. This is not a general observation and hence other
factors, of equal or greater importance, must also be present.
A prime question is the disposition of the valence electrons
of the metal. On this point Cubicciotti has been unclear,
stating first that these electrons are dispersed into the
energy bands of the entire melt (6) but later assuming that
they remain in the close vicinity of the parent atoms (7-10).

In the second theory, the metal atom ionizes to form the

normal cation of the salt plus electrons which occupy "anion vacancies". The latter, which might conveniently be called "electronide" ions, are similar to the F-centers proposed for the solid alkali metal halides and possibly related to the "solvated" electrons present in ammonia-alkali metal solutions. As more and more metal is dissolved, these electrons are said to interact to form a metallic conduction band, thus allowing for a smooth transition from an ionic lattice to a metallic one. Ukshe and Bukun (1) suggest that this description deserves to be more fully exploited.

The first two concepts thus differ only in the site of the valence electrons, one locating them on the metal atoms in the "cation lattice", the other in the "anion lattice". These concepts merge as the electrons are delocalized and distributed over the entire solution.

The third concept, is that dissolution of the metal is accomplished by the production of "lower" or reduced cations, i.e., a cation of lower oxidation state. Although proposed early, this view fell into disrepute amidst the many claims for the isolation of various subhalides. In most cases, these compounds were later shown to be finely divided mixtures of the normal salt and metal. However, more precise work has verified the existence of a number of these salts. Their isolation furnished strong support in returning this concept to favor. This view has the advantage of simplicity and is

probably supported by a majority of the workers in this field.

The metal-metal halide systems of the lighter lanthanides provide an unusual opportunity for the study and comparison of these concepts. A brief review of the pertinent features of their phase diagrams follows. The chloride and iodide systems for the elements La, Ce, Pr, and Nd were known at the time this thesis work commenced. More recently the metal-metal bromide phase diagrams for La, Ce, and Pr were determined.

The published phase diagrams for $LaCl_3$+La (11) and $CeCl_3$+Ce (12) show only a simple limiting solubility of metal ($\sim$9 mole % metal) with no formation of any intermediate solid phases. An earlier determination of the Ce diagram (13) is now considered to be in error. Although the isolation of $CeCl_2$ (14) has been claimed, in the writer's opinion the true composition of this compound is more likely to be $CeHCl_2$.

For the $PrCl_3$+Pr system (15), a greater solubility of the metal is observed ($\sim$19 mole % metal) and an intermediate phase (composition ca. $PrCl_{2.3}$) is formed. The latter is stable only at elevated temperatures, and disproportionates to the trichloride and metal upon cooling. While in another investigation (16) the existence of $PrCl_{2.3}$ was not noted, recent work (17) has confirmed the presence of this phase and has shown that it can be stabilized by small additions of Nd.

When the $NdCl_3$+Nd system (18) is considered, a further increase of metal solubility (to $\sim$30 mole %) is noted and

there is an almost embarrassing abundance of intermediate phases. A stoichiometric, incongruently melting dichloride exists, as well as two additional phases, also incongruently melting, whose compositions are $NdCl_{2.27}$ and $NdCl_{2.37}$.

The increasing metal solubility observed for this series and the ultimate appearance of stable lower halide salts has been interpreted as due to an increasing stability of the M^{2+} ion. The melting point depression of the trichlorides by the addition of metal does not contradict the assumed M^{2+} solute. However, recent measurements of the electrical conductivity of these melts (19-21) indicate that the true situation is considerably more complex since the La and Ce solutions show considerable electronic conductivity. In the Pr melts this electronic conductivity has decreased significantly while the Nd solutions show only ionic conductivity. To explain these data, one can postulate that "electronide" ions are produced in the La and Ce solutions or, as Bredig has suggested, assume an equilibrium between dispositive cations and electronide ions, thusly

$$M^{2+} \rightleftharpoons M^{3+} + (e)^{-}.$$
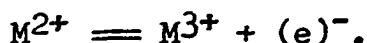
No measurement of solvent activity can differentiate between the dissolution of the metal to form a M^{2+} solute or to form a normal cation plus electrons (provided that these electrons behave as anions) or even a combination of these as three

"foreign" particles are formed per metal atom in each instance.

In general appearance, the recently determined MBr_3+M phase diagrams (22) are quite similar to the corresponding chloride systems. There are a few differences; the room temperature stability of $PrBr_{2.4}$ being the most significant. While the $NdBr_3+Nd$ phase diagram has not been determined as yet, it is almost certain that at least a dibromide will be found.

Consider now the MI_3+M systems for these same metals. Surprisingly, the phase diagrams do not resemble the corresponding chloride and bromide diagrams but they can be divided easily into two sets. In the first set are the phase diagrams of the La, Ce, and Pr systems (23). In each case there is a diiodide with a relatively high melting point (although only LaI_2 is congruently melting) and an intermediate compound whose composition is either $MI_{2.4}$ or $MI_{2.5}$. An increase in metal solubility is observed, but the limiting liquid compositions exhibit the unexpected trend $Pr < Ce < La$.

The single phase diagram for NdI_3+Nd (18) comprises the second set. In contrast to the chloride results only one lower phase is found melting congruently at a rather low temperature. This compound will be termed a diiodide although the composition is reported to be $NdI_{1.95}$.

Calculations based on the melting point depressions of

the triiodides and tribromides by added metal yield cryoscopic numbers less than three. But these differences may be due to the formation of primary solid solutions rather than different solute species.

The contrast between the corresponding chloride and iodide systems is striking, especially in the formation of the diiodides of La, Ce, and Pr. Even more unusual is the fact that these compounds appear to be electronic conductors (24), i.e., charge transfer occurs by the displacement of electrons rather than the migration of ions. Although previously unknown in the iodides, such behavior has been reported for other rare earth metal compounds in which the cation is nominally divalent. For instance, CeS (25) and LaC_2 (26) also exhibit electronic conduction with specific resistivities of 4×10^{-4} and 68×10^{-6} ohm-cm, respectively. In addition, the magnetic susceptibility of CeS indicates the presence of the Ce^{3+} ion. Consequently these compounds are believed to have a metallic conduction band and are formulated as CeS(e) and $LaC_2(e)$. On this basis it was postulated (24) that the "electronic" diiodides are more correctly represented as $MI_2(e)$.

On the other hand, all the lower halides of Nd are typically salt-like in being electrical insulators. One would then conclude that the Nd is present as a dipositive cation.

When the above experimental facts and their interpretations are pondered, several unanswered questions emerge. For

instance, what is the reason behind the abrupt change in electrical character between the solid diiodides of Pr and Nd, particularly since the rare earth elements usually have similar chemical properties? In the "electronic" diiodides, how free are the "conduction" electrons, i.e., is there any localization of the electrons on the cations? Would the choice of a different anion affect the electrical behavior of the metal solutions?

The following experiments were proposed in order to assist in answering these and other questions.

1. The magnetic susceptibility of the Nd dihalides would be determined to confirm unequivocally the electronic state of the Nd cation. While the electrical behavior of the solid dihalides and of the $NdCl_3+Nd$ melt pointed without much doubt to a dipositive cation, there remains a choice of electronic configurations, either $(4f^4)$ or $(4f^3 5d)$.

2. The magnetic susceptibility of LaI_2 would be measured in order to determine the extent, if any, of localization of the "conduction" electrons. This compound has several natural advantages. Because it is a congruently melting substance, preparation in reasonable purity is assured. More important, any localization to form a La^{2+} ion (which would be paramagnetic) would be much more readily observed against the diamagnetism of the La^{3+} and I^- ions. If CeI_2 or PrI_2 were used, one would be required to look for this effect in

the midst of already strongly paramagnetic ions.

3. In order to ascertain the nature of the conduction process in the "electronic" diiodides, their electrical resistivities would be determined as a function of temperature. A pure metallic behavior would be evidenced by a linear relationship with temperature while a pure semiconduction process is linearly dependent on the reciprocal of temperature.

After these experiments were under way, an invitation was extended by Dr. Bredig and his fellow workers at the Oak Ridge National Laboratory offering the use of their equipment to initiate the study of the electrical conductivities of the MI_3+M melts. The invitation was quickly and gratefully accepted. Because of a limitation in the available time, only two solutions, the Nd and Pr systems, were examined. The choice of these systems rather than some other combination was based on the premise, subsequently confirmed, that the conductivity of the La and Ce melts would rise rapidly beyond the range of the equipment and on the hope that more information could be gleaned from measurements made over a wider concentration range. In addition the behavior of the Pr and Nd solutions may possibly be pertinent to the explanation of the properties of the solid diiodides.

EXPERIMENTAL TECHNIQUES

General Considerations

As the materials used in these experiments are very hydroscopic and reactive, all operations were either carried out in an inert gas atmosphere or under vacuum conditions. Manual handling took place in an argon flushed dry-box with entry through an evacuable port. At all other times the materials were enclosed in glass (Pyrex or Vycor) containers.

These materials were analyzed by the following procedure. A sample was dissolved in H_2O and, for the dihalides, an amount of acetic acid just sufficient to dissolve the hydrolysis products was added afterwards. Any residue was removed by filtration and weighed. The filtrate was analyzed for the rare earth element by an EDTA titration using Arsenazo as indicator (27). Chloride was precipitated as AgCl while iodide was determined by a titration with $AgNO_3$ solution using eosin for the indicator. The reported halide to metal ratios are based on the analysis of the filtrate. Unless otherwise noted the amount of residue was < 0.2 wt. %, while material balances were $100.0 \pm 0.5\%$.

The various high temperature crucibles and certain other pieces of apparatus which were made of tantalum were fabricated from stock sheet and tubing. All welding was done using a D.C. arc in an apparatus (28) designed and built at this Laboratory.

The wiring (usually thermocouples) leading from the samples to exterior points were passed through the glass envelopes using Stupakoff lead-throughs (Carborundum Co.) soldered to Kovar glass-to-metal seals.

Preparation of the Trihalides

The anhydrous trihalides were prepared by the reaction of the pure metal with either elemental iodine or with hydrogen chloride gas using the methods developed earlier by Druding (15, 18). The resulting products had the appearance and texture of colored asbestos. All the trihalides except LaI_3 are highly colored, although at this stage the colors were somewhat dull. With two exceptions, all the trihalides were then sublimed or distilled under vacuum in order to remove any non-volatile impurities, which were presumed to be largely oxides or oxyhalides.

The sublimation/distillation step was considered important when the material was to be used in the measurement of electrical resistivities or conductivities. Only the trihalides used in the preparation of the neodymium dihalides were not sublimed, for reasons that will be discussed later. The sublimed material consisted of many small crystallites and could easily be ground to a powder in contrast to the crude material. The analytical samples dissolved easily in water with no visible cloudiness. The halide to metal ratios were invariably 3.00 ± 0.01.

An apparent instability of NdI_3 at high temperature has been noted (29) and evidence for a similar behavior in all these triiodides was found during the sublimation/distillation step. When the process was carried out in an all tantalum apparatus, a dark, almost black material was observed which fortunately was more volatile than the triiodides, condensing some distance away. Later heating of this material in air yielded fumes of iodine and a whitish residue; hence the substance was likely some iodide of tantalum. When a Vycor apparatus was used, side reactions were also noted. A volatile, pinkish (from traces of iodine?) material was found with a melting range of 125-135°. This material fumes in air and qualitative tests showed that it also contained iodine. On this basis, it was inferred that this compound was SiI_4 (m.p. 121°). Although the residue from the sublimation usually adherred tightly to the Vycor walls, a light, silvery, nonadherent substance was collected from a slow sublimation of PrI_3. Analysis indicated that the material was mostly PrOI (wt. % Pr: found-47.9, theory-49.6; wt. % I: found-43.9, theory-44.6). In as much as tantalum can hardly be considered a strong reducing agent, it appears that the triiodides disproportionate into as yet unknown species.

Preparation of the Neodymium(II) Halides

Both dihalides were prepared by equilibration of the appropriate trihalide with excess Nd metal. The only

difference occurred in the programming of the temperature.

First an excess of the metal was melted under vacuum in a tantalum crucible made from 0.75 inch i.d. tubing. Although the fusion of the metal reduced the available surface area for reaction, this was compensated by the resulting ease in which the salt and metal phases were later separated. A suitable quantity of the trihalide was then added, the container evacuated, and then dry He was admitted until the pressure reached ⌣30 mm Hg. The inert gas served to reduce the volatility of the trihalide.

In the synthesis of the dichloride, the reactants were heated to ⌣ 860° and maintained at this temperature for 12 hours. At this temperature Nd metal is the only solid phase in equilibrium with the melt and the reduction is greatly facilitated. The temperature was then lowered below the melting point of $NdCl_2$ (to ⌣825°) and the reduction continued for an additional six hours, following which the product was quenched. An analysis of the product gave a Cl/Nd ratio of 2.04 ± 0.01. Because rates in the attainment of solid-solid equilibria are slow, attempts to obtain a more completely reduced material were not made.

For the preparation of the diiodide, the reactants were first heated to slightly above 800° for several hours in order to fuse the triiodide and start the reduction. Afterwards the temperature was gradually lowered to ⌣580° (just above the

melting point of the diiodide) and the equilibration was
continued until a total of 12 hours had elapsed. After
cooling, the composition of the product was determined to be
$NdI_{1.95\pm0.01}$ in agreement with the data of Druding (18).

These long equilibration times were necessary due to the
relatively viscous nature of the Nd solutions. Druding (15),
in his determination of the phase diagram, had also noted this
behavior. Further evidence was later found when the conduc-
tivities of these melts were measured; the dissolution of Nd
occurred at much slower rates than that of Pr.

As stated earlier, the unsublimed trihalides were used in
the preparation of these dihalides. The reason is simply that
the magnetic susceptibility measurements on these compounds,
the first experiments to be performed, were essentially com-
pleted by the time sublimation of larger quantities of the
trihalides became a routine procedure. Had they been avail-
able, the purer materials would have been used.

A decision not to repeat this work was based on this
reasoning. First, almost all the impurities (i.e. oxy
compounds) in the trihalides do originate with the metal.
This was illustrated by an analysis of the crude $NdCl_3$ where
600 ± 100 ppm by weight of oxygen was found. Calculation
showed that this concentration was compatible with the total
amount known to have been present in the metal used in the
trichloride synthesis. Therefore, such impurities would be

reintroduced by the reduction with metal. The concentration would, of course, be reduced if only a stoichiometric amount of metal had been used. However, an appreciable excess is preferable in order to maintain an adequate surface reaction area. Second, the amounts of impurities estimated to be present (~ 1 wt. % as NdOI) was not thought to be great enough to alter the results significantly. This view is supported by the nearly identical results obtained for $NdCl_{2.04}$ and $NdI_{1.95}$ despite the difference in stoichiometry of these compounds.

Preparation of the 'Electronic' Diiodides

As with $NdI_{1.95}$, these diiodides were prepared by the reduction of the corresponding triiodides with metal. But there were special considerations. The impurities which were relatively unimportant in the magnetic susceptibility determinations could have a much larger influence on the resistivity measurements, and efforts were made to reduce these to as low a concentration as possible. In addition, two of these diiodides are incongruently melting; thus incomplete reduction and the retention of other iodide phases also presented problems.

Unfortunately these diiodides can not be purified by a vaporization process because disproportionation to the metal and gaseous metal triiodide occurs. This meant that any purification had to occur during the solid-liquid

transformation. Assuming that no solid solutions are formed, a pure compound should be deposited when the molten solution is slowly solidified by a passage through a thermal gradient. Any impurities should theoretically remain in the liquid until the latter's final disappearance.

To this end, a 15 inch Marshall furnace was modified so as to have a rather sharp thermal gradient within it. The construction details are shown in Fig. 1. The inner diameter of the furnace was large relative to the sample container and in order to reduce convection currents, extra material, consisting of baffles and a divided tube, was placed in the cavity. The top portion of this tube was made of stainless steel in order to produce a large region in which the temperature was as nearly uniform as possible, while the bottom was of alumina so as to reduce thermal fluctuations to a minimum. Such fluctuations at the solid-liquid interface could precipitate the metal which might not redissolve.

The electrical heating element of this furnace is tapped at convenient intervals so that the power consumption in any one section can be easily altered by means of external shunts. A temperature gradient of between 7 and 10° per cm. (at 800-900° furnace temperature) was obtained just below the junction of the steel and alumina tubes when a 25 ohm power resistor was in parallel with the bottom seven inches of the furnace windings.
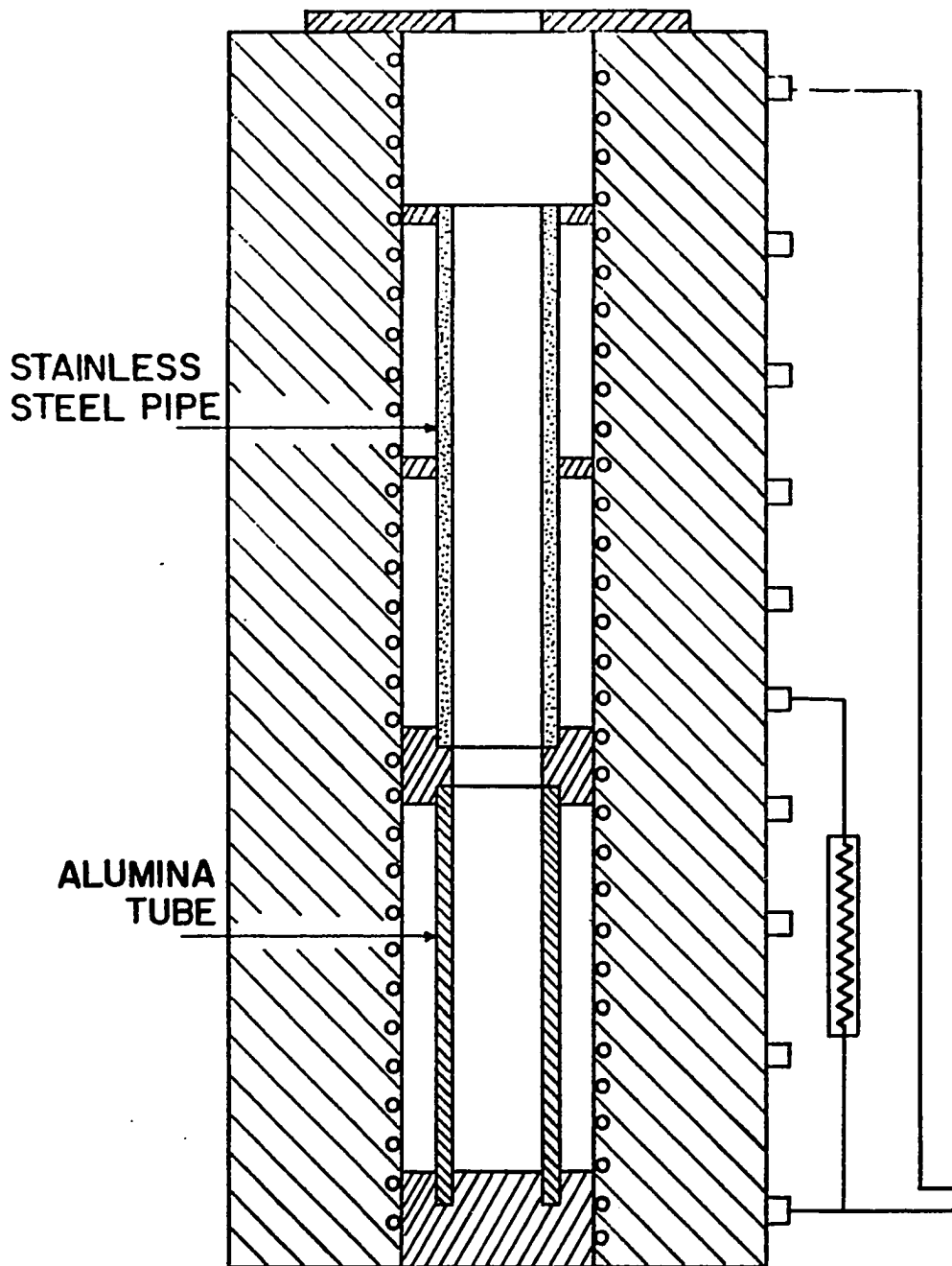
STAINLESS
STEEL PIPE

ALUMINA
TUBE

Fig. 1. Cross-sectional view of the Marshall furnace as
modified for the growing of MI_2 resistivity
specimens.

Specimens of the diiodides were cast in the form of 0.25 inch rods (for reasons to be discussed later in connection with the description of the resistivity apparatus). Since complete reduction of LaI$_3$ does occur in the liquid phase, the preparation of LaI$_2$ specimens was relatively simple. A container was fabricated from tantalum tubing (0.25 inch diameter and 0.010 inch wall thickness) with the length or height between five and seven inches. The container was heated at 1000° for an hour in high vacuum with the result that the tantalum surfaces became much cleaner in appearance. A calculated excess of the La was added and melted, again under high vacuum. After the sublimed LaI$_3$ had been added and tamped into place, the empty upper end of the tubing was pressed flat and later welded shut.

Some exposure to the room atmosphere occurred when the loaded tantalum tube was transferred to the welder. However, the probability that significant amounts of moisture reached the LaI$_3$ was extremely low since diffusion would have had to occur along the narrow path between the pressed sides of the tubing. Any partial intrusion into this path would be quickly removed during the evacuation of the welding chamber.

After sealing, the sample was heated within an evacuated Vycor container in the upper half of the Marshall furnace and equilibrated above 830° for at least 24 hours. Temperature was measured by a thermocouple attached directly to the bottom

of the tantalum tubing. Afterwards, the electrical power to
the furnace was adjusted until the temperatures in the upper
and lower parts bracketed the melting point of LaI_2. Then the
sample was manually lowered through the thermal gradient at a
rate of ~0.5 inch/hour in ~0.2 inch steps.

The LaI_2 specimen was removed from its tantalum container
by peeling the metal in a manner similar to that used in
opening coffee cans. With proper care, specimens between one
and three inches in length were obtained.

Portions of the different specimens were analyzed and
their compositions were between $LaI_{2.00}$ and $LaI_{2.04}$ with only
minor amounts (~0.2 wt. %) of either oxy compounds or free
metal. Resistivity measurements were made only if the
composition was $LaI_{2.00\pm0.01}$.

Unfortunately the relatively straight-forward method
described above can not be applied to the synthesis of
coherent rods of pure CeI_2 or PrI_2 because complete reduction
to the diiodide is not attained in the liquid phase. Long
equilibration with stoichiometric quantities of the triiodides
and metals might have produced the desired diiodide but there
would be no possibility for removing any extraneous phases.
And such equilibrations would be hindered by the small
diameter/length ratio of the containers.

Two methods were devised in attempts to circumvent these
problems. In one, a special tantalum container, shown in

Fig. 2, was made from 0.75 and 0.25 inch diameter tubing.
Excess metal was melted in the upper ring-shaped reservoir.
A quantity of triiodide sufficient, when molten, to cover the
protruding inner portion of the smaller tubing was added.
Thermocouples were attached to the bases of both sections and
the sample was heated, again in the upper portion of the
Marshall furnace, to 500°, with continuous pumping. Then argon
was added until the pressure was ∽30 mm Hg. Heating was
continued until the temperature was slightly above the incon-
gruent melting point of the diiodide (808° and 758° for the Ce
and Pr systems, respectively). The samples were equilibrated
at this temperature for 16 hours and then were gradually
lowered through the thermal gradient.

Theoretically, as the solution temperature reaches the
melting point of the diiodide, the latter solid separates
leaving the solution locally richer in triiodide. The local
solution should be reduced to the limiting value by diffusion
from the upper reservoir and hence the reduction to the pure
diiodide should be accomplished without the inclusion of
other phases. Unfortunately the theoretical results were not
obtained. When the rate of lowering was greater than about
0.25 inch per hour, very little reduction beyond the equilib-
rium composition of the liquid occurred and a mixture of
iodide phases resulted. One sample of $PrI_{2.07}$ was made by
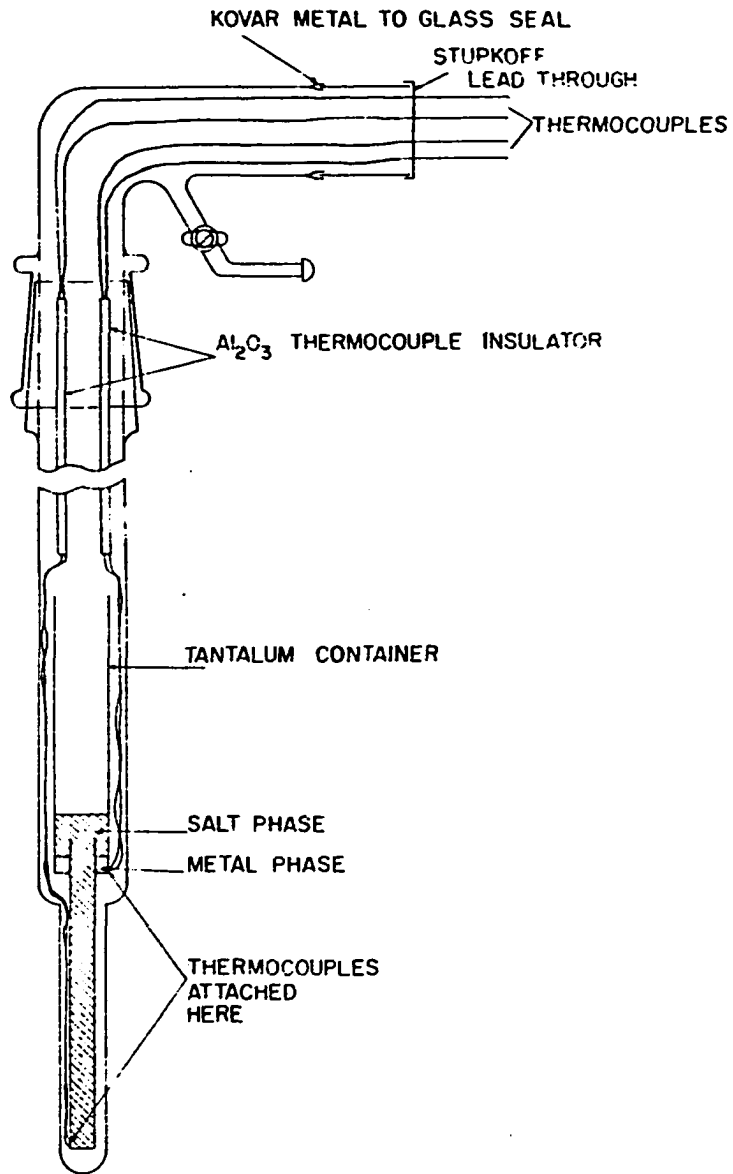using a slower rate (0.1 inch per hour). When compared to

Fig. 2. Schematic view of the apparatus used for the preparation of CeI_2 and PrI_2 resistivity specimens.

the limiting liquid composition, $PrI_{2.12}$, it is probable that even slower rates would be beneficial. However, the analysis of these materials indicated that the amount of water-insoluble residues (i.e. oxy compounds or metal) generally increased as the rate of growth decreased, and one thus reaches an impasse.

A possible reason for the sluggish reduction was thought to be the long diffusion path from the metal phase to the solid diiodide. In an effort to counteract this, one specimen was made by the following method. A long narrow rod of Pr metal was independently suspended in the reduced melt with its lower end only a short distance from the solid-liquid inter-face. The details of the apparatus are shown in Fig. 3. The central Vycor tube kept the thermocouple wires from interfering with the suspension of the metal rod. As the sample was lowered through the thermal gradient (at a rate of ⌒0.1 inch/ hour), the suspended Pr metal was adjusted with the winch so as to maintain a constant position with respect to the furnace. The separation of the Pr metal and the diiodide surface was about 0.25 inch, a spacing that was verified at random intervals by temporarily lowering the rod since the suspension cable visibly relaxed when the solid surface was reached. The growth rate may have been too slow for an analysis of material from the lower end yielded an I/Pr ratio of 1.89 ± 0.01 with a residue of approximately three weight
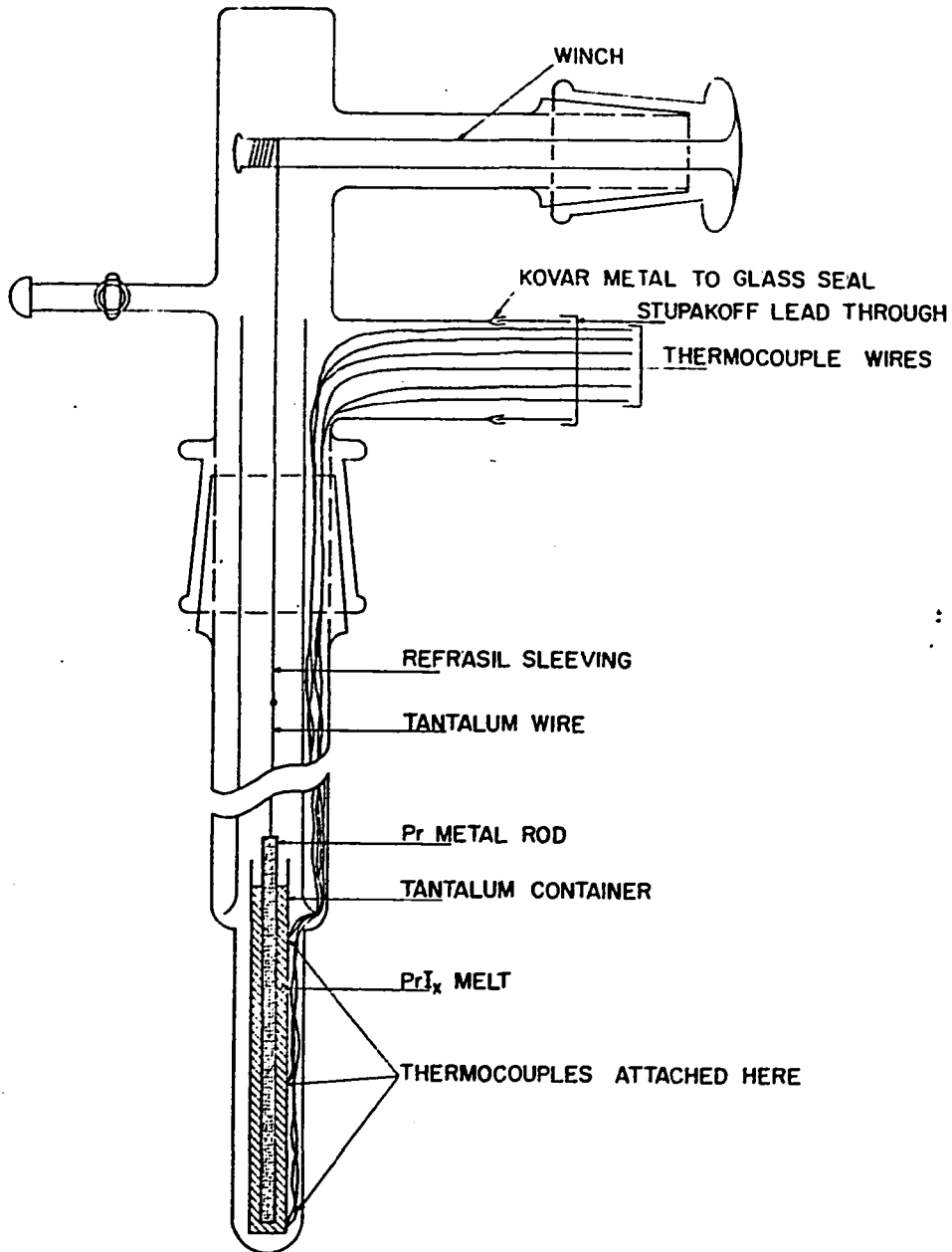
Fig. 3. Schematic view of the alternate apparatus used in the preparation of a PrI_2 resistivity specimen.

per cent. Little change in the appearance of the residue was observed when it was allowed to stand for several days in the room atmosphere; a fact that indicated the composition was largely oxy compounds. The method is applicable only to the Pr system because the melting point of CeI_2 is greater than that of Ce metal.

The magnetic susceptibility of LaI_2 was measured on material that was prepared in the same manner as $NdI_{1.95}$, i.e. reduction of the molten salt solution with excess metal above the melting point of LaI_2. The solid product analyzed as $LaI_{2.03\pm0.01}$ with 0.3 wt. % residue.

Determination of Magnetic Susceptibilities

The susceptibilities were calculated from the apparent change in weight brought about by the application of a magnetic field, i.e., the classical Gouy method. The apparatus has been described in earlier theses (30, 31, 32) and the reader is referred to these for details. In brief, a four-inch, single-yoked, water-cooled electromagnet was used, riding on steel rails so that it could be moved without disturbing the rest of the equipment.

The magnetic field strength could be varied continuously by the adjustment of the electrical current. The latter was regulated electronically so that current fluctuations were reduced to about 0.2 milliamps over the entire range (0 to 10 amps). The field strength was determined by detection of the

resonance frequency of protons in H_2O using a Pound magneto-meter. Accurate measurement of the frequency was accomplished by beating the magnetometer frequency against the output of a signal generator. The inhomogenuity of the field was about 0.1 per cent.

The Gouy tubes were made from precision bore Pyrex tubing, 0.2517 or 0.1810 ± .0002 inch diameter, 18 inches in length (Wilmad Glass Co., Inc.). A glass septum 7 inches from one end divided the tubes into two sections. A male 10/30 ground glass joint was added to the end of the longer (sample) section. With this design of the Gouy tube, the correction for the diamagnetism of the glass was eliminated since equal and opposite forces would be exerted on walls as the tube passes completely through the magnetic field grad-ients. However each tube was checked in the apparatus before loading to verify this. With no tube was a detectable (0.1 mg) change in weight observed.

The finely ground samples were packed into the Gouy tubes as follows. An amount of the sample sufficient to fill the tube to a depth of between 1/8 and 3/16 inch was added. This material was tamped with a glass rod in a consistent, repeated manner, and then another addition was made. Tamping and addition of material alternated until a height of 8 to 9 inches had been reached. The Gouy tube was then capped by a female joint with attached vacuum stopcock. The tube was

<u>very</u> gradually evacuated and then sealed by collapsing the glass wall in the region between the sample and glass joint with a hand torch. The height of the sample was measured with a cathetometer while its weight was determined from the weights of the Gouy tube and joint before and after filling. The correction for bouyancy was negligible.

The Gouy tubes were suspended from an analytical balance and within a copper tube. Temperature was measured by chromel-alumel thermocouples mounted at intervals on the exterior of this tube. During the experiments the tube was integral with the balance case and both were slowly and continuously flushed (except when weighing) with either helium or dry nitrogen gas.

A mineral oil bath surrounded the copper tube and was heated by means of two heating tapes wrapped around the bath walls, one above and one below the poles of the magnet. The electrical power to each heater was individually regulated by a variable transformer (Powerstat). Measurements were taken at room temperature and above with readings taken at convenient intervals during both the heating and cooling periods.

The low temperature measurements were made later after the apparatus had been modified by the substitution of a Dewar assembly (30) for the mineral oil bath. The sample was first cooled to 78°K with liquid nitrogen using He gas as the heat transfer agent. After

measurements had been made at this temperature, the sample was thermally isolated from the liquid nitrogen bath and was slowly warmed by the passage of the helium gas. If a faster heating rate was desired, a small resistance heater attached to the bottom of the copper tube was turned on. Measurements were made at convenient intervals until room temperature was reached. The complete run took about 6-8 hours. Temperature was measured using calibrated copper-constantan thermocouples.

Measurement of the Conductivities of Metal-Salt Melts

For these measurements, the equipment built and assembled for M. A. Bredig and his co-workers at the Oak Ridge National Laboratory was utilized. The equipment and the experimental procedures have been completely described in the literature (19, 20, 33). Suffice to say that the conductivities of the pure salts were measured with a capillary cell while those of the metal solutions were determined using parallel molybdenum electrodes. The capillary cell is normally made of single crystal alumina (Al_2O_3), but for these measurements one of magnesium oxide (MgO) was inadvertently supplied. The consequences of this accidental substitution are discussed later with the experimental results.

Resistivity Measurements on the Solid Diiodides

Because it was hoped that the resistivities of the "electronic" diiodides could be measured over an extended

temperature range, the construction of the sample holder was
of prime importance. Its design was hampered by several
restrictions. Some rough preliminary measurements had indi-
cated that the resistivities were of the order of milliohm-
centimeters or less. Hence it was preferable that the
specimens have a large length-to-area ratio in order to
obtain voltages that could be conveniently measured. However,
these substances are not very strong and clearly could not be
cast as slender rods. In addition the inherent reactivity of
these compounds, especially at the higher temperatures,
dictated that there be a minimum of contact with the sample
holder, i.e., that the specimens be self-supporting. As the
best compromise to these considerations the specimens were
cast as 0.25 inch rods.

In the first attempt at constructing a suitable holder,
copper was extensively used and the various parts were
electrically insulated by Transite and glass spacers. The
potential probes were supported within a piece of Vycor tubing
and were aligned by holes drilled ultrasonically through the
glass walls. However, a trace of oxidizing gases, possibly
from the porous Transite, reacted with the diiodide specimens
liberating elemental iodine. At moderate temperatures the
latter provided an altogether too convenient means for the
gaseous transport of copper with the result that thin films
were deposited all over heated portions of the apparatus and

the sample. Efforts to eliminate this transport proved
futile.

A second and successful holder is illustrated in Fig. 4.
The main body is of Lavite (Maryland Lava Co.), a rather
versatile synthetic magnesium silicate. In the unfired state
this material can be machined very easily but becomes hard and
strong when heated in air at temperatures $>1000°$. The
diiodide was supported by the hollowed ends of stainless steel
rods which were threaded into machined holes in the Lavite and
which also served as the power connections to the sample. The
supports for the potential probes, likewise of stainless
steel, were also threaded into their own holes. Such thread-
ing permitted the positions of these supports to be easily
adjusted.

A thin sheet of tantalum metal separated the sides of the
steel support and the diiodide specimen as a precaution
against their possible reaction. In addition it proved
necessary, in order to obtain good electrical contact, to
insert a small circular slab of the appropriate rare earth
metal between the end of the specimen and its support.

The potential probes were made from tungsten electrodes
(Heliarc, Linde Company) and their tips were ground to sharp
points. Each probe was inserted into a narrow hole drilled in
a small cylinder of stainless steel. These cylinders nestled
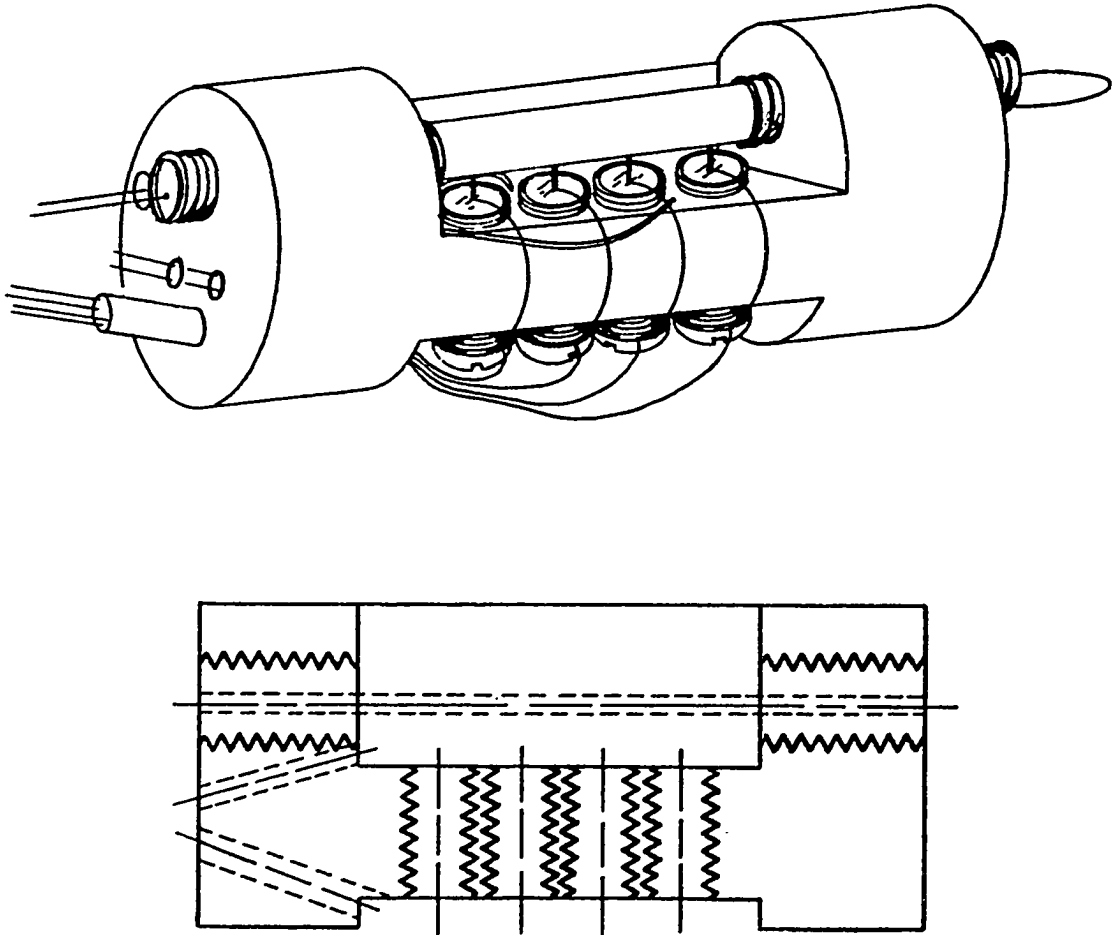snugly in the hollowed ends of the threaded supports. In

Fig. 4.   The specimen holder.   (Upper) A perspective view.
(Lower) A cross-sectional view of the Lavite block.

retrospect, the cylinder and its support might just as well have been a single piece. The original design allowed for the insertion of springs beneath the cylinders so that the probes would exert continuous pressure against the specimen. Unfortunately, springs that were useable over an extended temperature range were not available.

In order to assure electrical continuity, a silver wire was welded to the tungsten probe. This wire led to the opposite end of the steel support where it joined another silver wire connecting with the external circuitry. This junction permitted the easy replacement of the probes.

The temperature was measured by two chromel-alumel thermocouples, one near each end of the specimen. These thermocouples were also used to measure temperatures below 200°K although d(EMF)/dT decreases appreciably below this point.

After the sample holder and its electrical connections had been assembled for the first time, it was heated to 500° for 48 hours under continuous vacuum (with Hg diffusion pump) in order to remove any oxidizing gases from the porous lavite. From then on, the apparatus was hendled only in the drybox. When exposure to the air did occur, the above treatment was repeated before any specimens were inserted.

In the first trials, direct current was used rather than alternating current in order to take advantage of the simpler

instrumentation. However, rectifying characteristics were observed soon after any measurement was begun as apparently a thin layer of insulating material formed at the metal-diiodide interface. At the higher temperatures, the coating became visible. Once a sufficiently heavy layer was formed so that an x-ray powder pattern could be taken on material scraped from the surface; surprisingly, the triiodide was found to be a major component.

These difficulties prompted a change to A.C. techniques which reduced but did not eliminate them. A sinusoidal wave form was not consistently obtained from the potential probes until the respective rare earth metal was used as the power contacts. If the formation of the triiodide at the interface were truly the correct explanation for the observed rectification, then one might infer that, in the presence of the rare earth metal, the diiodide would be formed instead.

The circuitry of the external electronic equipment is shown as a block diagram in Fig. 5. The output of the oscillator (Hewlett-Packard Model 200CD) was fed to a power amplifier (Heathkit Model AA-81). Its output was sent consecutively through a milliameter, a 'standard' resistor, and the diiodide specimen. Potential leads from both the specimen probes and the 'standard' resistor went to a switch box from which the desired signal was sent to the input of a low-noise, battery operated differential preamplifier (Tektronix Type
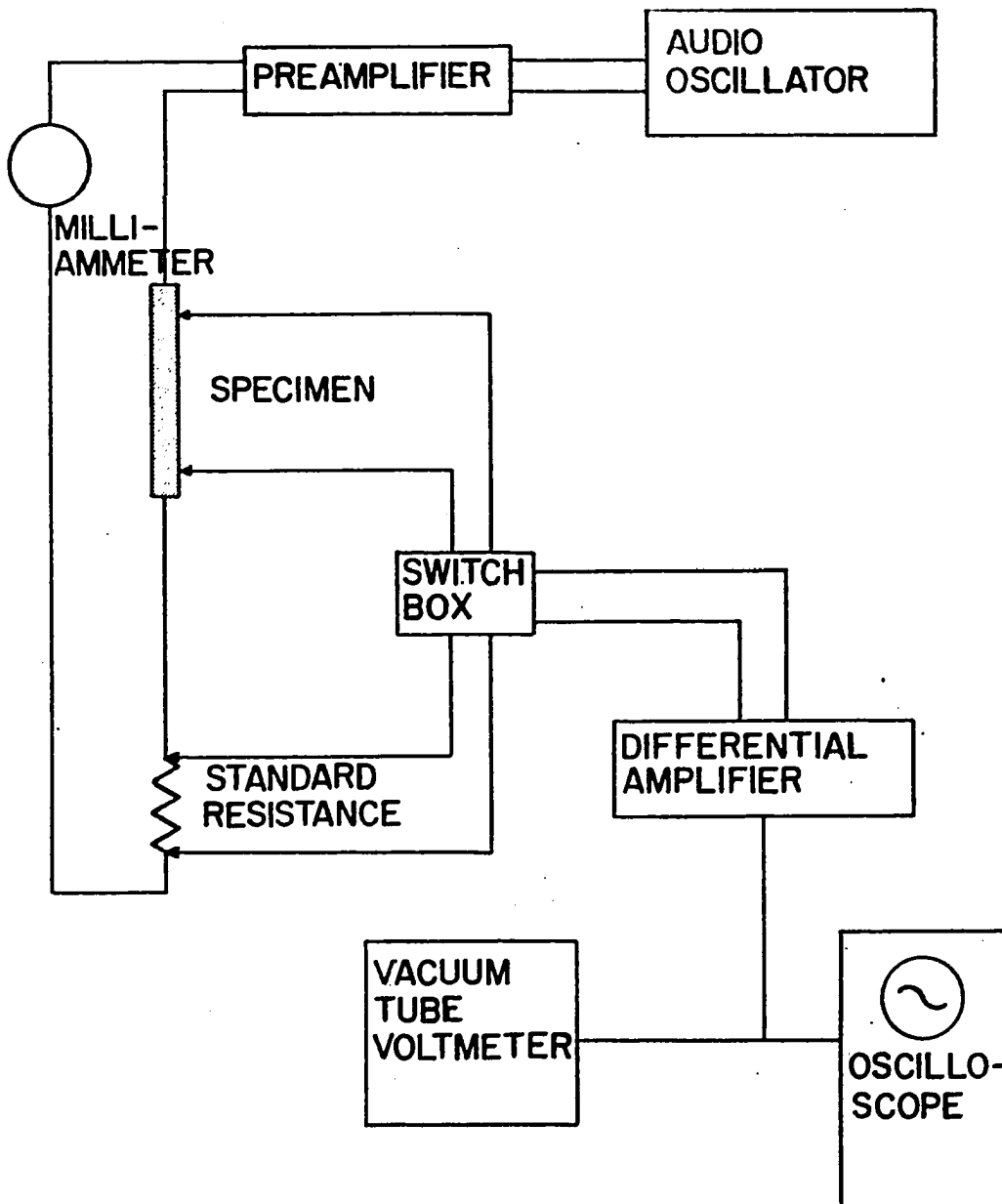
Fig. 5. A block diagram of the electrical circuitry used for the determination of electrical resistivities.

122). The output was measured with a vacuum tube voltmeter
(Hewlett-Packard Model 400H) while simultaneously the waveform
was monitored on an oscilloscope connected in parallel.
Shielded wires were used for all external wiring in order to
reduce the noise level to a minimum. The 'standard' was a
short piece of copper wire the resistance of which was deter-
mined by comparison with a standard ten milliohm shunt using
both D.C. and A.C. methods.

Measurements were made at low temperatures by immersing
the specimen holder (within its evacuated glass envelope) in
a liquid coolant contained in a vertical Dewar. The coolant
was either liquid nitrogen, Dry Ice-acetone slush, or an
aqueous $ZnCl_2$ solution (eutectic composition) which had
initially been cooled by a Dry Ice-filled glass cylinder.
Temperatures greater than ambient were reached by inserting
the evacuated holder in a horizontal furnace which had a
grounded inner lining of Inconel to eliminate inductive
electrical noise.

The resistance of the specimen was calculated from the
resistance of the 'standard' and the ratio of their probe
potential using the equation

$$R_{spec.} = \frac{V_{spec.}}{V_{stnd.}} R_{stnd.}$$

With this value plus the radius of the specimen and the probe

separation, the resistivity of the specimen was determined
from the equation

$$\rho = R_{spec.} \ \frac{\pi r^2}{L}.$$

MAGNETIC SUSCEPTIBILITIES

To the chemist, the value of the magnetic susceptibility lies in its relationship to the electronic structure of the elements and their compounds. Nominally, a substance is termed diamagnetic or paramagnetic depending whether the sign of the susceptibility is negative or positive. This definition is generally acceptable even though every material possesses some inherent diamagnetism arising from the orbital motion of its electrons. Paramagnetism, when present, is usually of greater magnitude and is always associated with the presence of unpaired electrons.

The localization of unpaired electrons on a particular atom or ion confers on that body a permanent magnetic moment which is a function of the electron states. For the rare earth cations, van Vleck (34) has derived a theoretical expression (Eqn. 1) relating these electron states in terms

$$\chi_p = N \sum_{J=|L-S|}^{|L+S|} \frac{[g_J^2\beta^2 J(J+1)/3kT + a_J](2J+1)e^{-E_J/kT}}{\Sigma(2J+1)e^{-E_J/kT}} \tag{1}$$

of the vector representation of their spin and orbital moments, S and L, to the paramagnetic portion of the molar susceptibility, χ_p.

In Eqn. 1 β is the magnitude of the Bohr magneton, J is the vector sum of the S and L, g_J and E_J are the Lande

splitting factor and energy of the state J and α_J is given by

$$\alpha_J = \frac{\beta^2}{6(2J+1)} \left[\frac{F(J+1)}{E_{J+1}-E_J} - \frac{F(J)}{E_J-E_{J-1}} \right]$$

where $\quad F(J) = \frac{1}{J} \left[(S+L+1)^2-J^2 \right] \left[J^2-(S-L)^2 \right]$.

This derivation assumes that the atomic moments act independently of one another, a condition that is particularly well satisfied by the rare earth metal cations.

When, as frequently happens, the excited states are energetically widely separated from the ground state, this expression reduces in form to the empirical Curie law in which χ_p is inversely proportional to the temperature.

The proportionality factor is known as the Curie constant and its theoretical value, by comparison to the first term of Eqn. 1, is given by

$$C = (\frac{N\beta^2}{3k}) g_J^2 J(J+1) \tag{2a}$$

or $\qquad C = (\frac{\mu}{2.84})^2 \text{ erg-gauss}^{-2}\text{-mole}^{-1}\text{-sec.} \tag{2b}$

Eqn. 2b is obtained by replacing the constants with their numerical values and by defining μ as $g_J\sqrt{J(J+1)}$. For a given combination of electrons, the J value of the ground state, and thus its magnetic moment, can be predicted from Hund's Rules.

More commonly, however, the actual behavior is better

described by the Weiss modification of the Curie law (Eqn. 3) in which the effect of factors such as interatomic inter-

$$\chi_p = \frac{C}{T + \Delta} \qquad (3)$$

actions or the crystalline field is approximated by the Weiss constant, Δ.

In order to obtain the molar paramagnetic susceptibilities of the rare earth metal cations, the diamagnetic contributions of all the ions were subtracted from the experimental results using the values suggested by Selwood (35). These are (in 10^6 erg-gauss^{-2}-mole^{-1}):-26 for Cl^-, -52 for I^- and -20 for M^{3+}. The value for Sm^{2+}, -23, was used for the Nd^{2+} ion.

The experimental molar susceptibilities were calculated from the measured weight changes using Eqn. 4, the derivation of which may be found in almost any standard physics text.

$$\chi_M = 2g(\frac{h}{w})M(\frac{\Delta w}{H^2}) \qquad (4)$$

The various quantities are:

g - the gravitational constant whose value, 980.3 cm/sec^2, was determined by other personnel of the Laboratory,

h - the height of the sample in cm.,

w - the weight of the sample in gm.,

Δw - the change in weight produced by the magnetic field,

M - the molecular (formula) weight of the compound

    calculated on the basis of the halide/metal

    ratio, and

H - the magnetic field in gauss.

Neodymium(III) Halides

The experimental data for $NdCl_3$ and NdI_3 are tabulated in Appendix A as well as the calculated paramagnetic susceptibilities of the Nd^{3+} cation. The latter are also shown in Fig. 6 as a function of temperature.

There is little dependence of the susceptibility on magnetic field strength when H is greater than 3 to 4 kilogauss. Below this value, however, χ increases somewhat in magnitude as H decreases. This effect may be due to instrumental errors.

The behavior of each trihalide can be adequately represented by a Curie-Weiss equation in which the constants $(C;\Delta)$ were determined by a least squares analysis to have the values (1.769;31°) and (1.716;9°) for $NdCl_3$ and NdI_3, respectively. The corresponding magnetic moments, μ, are 3.78 B.M. and 3.72 B.M. (estimated error is $\pm$ 0.05 B.M.) which may be compared to the theoretical value of 3.62 B.M.

The only previously published data for these compounds are those of Sanchez (36) for $NdCl_3$ which are also shown in Fig. 6. His reported values for the constants $(C;\Delta)$ are (1.861;57°) from which μ calculates to be 3.87 B.M. Although
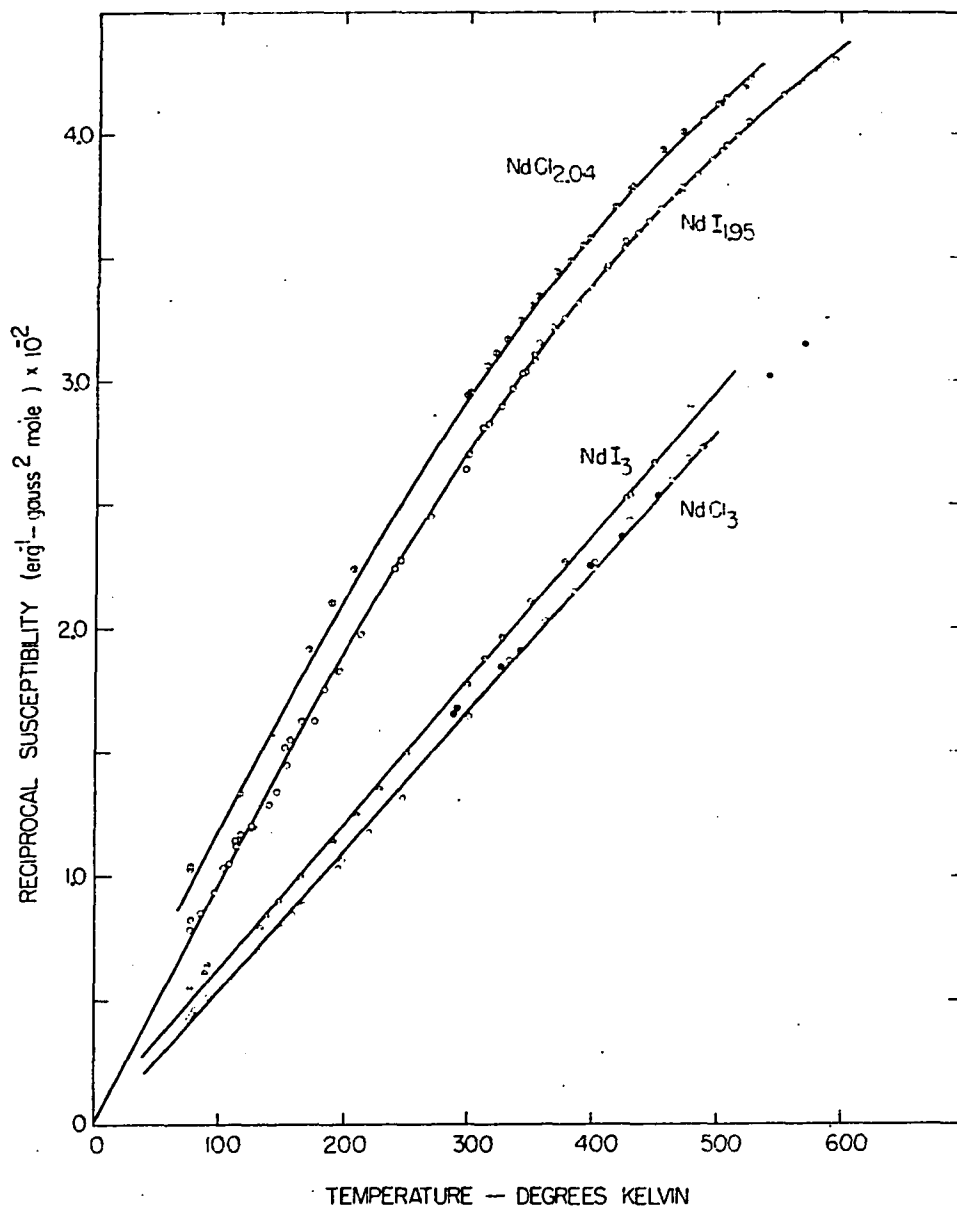
Fig. 6. Reciprocal paramagnetic susceptibilities of the Nd
halides. For clarity, the data for $NdCl_3$ has been
displaced downwards by 0.1 units while that for
$NdCl_{2.04}$ has been displaced upward by 0.1 units.
The solid circles (•) are the data of Sanchez (36)
for $NdCl_3$.

the derived equations seem to differ, the present data vary significantly from those of Sanchez only at room temperatures. At all other common temperatures the experimental susceptibilities agree quite well. Hence the differences in the empirical equation can be considered the result of the shorter temperature range (289-572°K) of the earlier work.

The data for NdI_3 are of interest primarily in regard to the magnitude of Δ. With many Nd compounds, Δ ranges between 40° and 60° with the smaller values possessed by those compounds which are magnetically dilute (35). Thus in NdI_3, those factors which are normally present in Nd compounds must either be of much less importance or act in opposition to one another.

Neodymium(II) Halides

The numerical data are listed in Appendix B with the calculated paramagnetic susceptibilities for the Nd^{2+} ion also being shown in Fig. 6. As in the trihalides, there is a small increase in susceptibility when H < 3 kilogauss.

It is at once apparent that the Curie-Weiss equation is not obeyed by these compounds although there is an asymtotic approach at lower temperatures. In this respect these compounds are similar to those of Sm^{3+} and of Eu^{3+} where this behavior is caused by the populating of low lying excited states.

The curves for $NdCl_{2.04}$ and $NdI_{1.95}$ are almost

superposable and while the following calculations were based on the $NdI_{1.95}$ data (which was more complete at the lower temperatures), the results are applicable also to $NdCl_{2.04}$.

A straight line was drawn through the approximately linear low temperature results and from the slope the moment was calculated to be approximately 2.8 B.M. which compares with 2.68 B.M. predicted for four unpaired 'f' electrons. A moment of 4.63 B.M. would be predicted for the $(4f^3, 5d^1)$ arrangement from Hund's rules. However, to preserve scientific honesty, it must be admitted that the orbital contribution of the 'd' electron to the total moment would probably be quenched, i.e., have a time-averaged value of about zero, and in this case, the total moment would also be 2.68 B.M.

Although an unambiguous choice is not strictly possible if based solely on the low temperature data, the presence of the low lying excited state is strong evidence for the $4f^4$ configuration which is expected, from theoretical considerations (34), to have such states. In addition there is the historical argument, known as Kossel's rule, that non-trivalent rare earth cations have the electron configuration of the adjacent isoelectronic M^{3+} ion.

In attempts to fit the susceptibility data to the theoretical expression of Van Vleck (Eqn. 1), it was assumed that only the ground state and the first excited state would be appreciably populated at the experimental temperatures. In

addition the level degeneracies were assumed to be 9 and 11

for ground and excited states respectively, i.e., the

corresponding J values were 4 and 5.

With the energy separation, ΔE, as the sole parameter,

only rough correlations with the observed data were obtained.

However, when the moments of the two states were also used

as parameters a very satisfactory fit was quickly attained.

While it might be argued that there was some inconsistency in

this approach in as much as the level degeneracies were left

unchanged (i.e., J values were assumed), these may have

integral values only and the moments must necessarily change

drastically to merit any such changes. By successive approxi-

mations, the following values for the parameters were obtained:

$$\Delta E/k = 1400^\circ K$$
$$\mu_g = 2.87 \text{ B.M.}$$
$$\mu_e = 5.36 \text{ B.M.}$$

The theoretical moment for the excited state is 4.93 B.M. and

hence the moments of both the ground and excited states are

about 7-8% greater than theoretical compared to ∼4% in the

case of the trihalides. The lines drawn through the dihalide

data in Fig. 6 were calculated from Eqn. 1 using the above

parameters.

The fluorescent spectra of the isoelectronic Pm^{3+} ion was

recently investigated (37) and the energies of many excited

levels were calculated. The first excited state was calculated to lie 750°K above the ground state. No direct observation was made of this level, its energy arising out of a matrix representation that was compatible with the observed lines. Even so, the agreement can be considered satisfactory since the difference may be a result of the different nuclear charges.

Of major significance is the fact that the $4f^4$ configuration can now be studied in a more convenient, though chemically reactive, compound. The state was previously available only with the rare and radioactive promethium salts.

Lanthanum Diiodide

The susceptibility data for $LaI_{2.03}$ is tabulated in Appendix C. Measurements were made only at room temperature (288°K) and at 78°K. The observed susceptibilities were quite small and depended on the magnetic field strength. The dependence is approximately linear in (H^{-1}) and thus there may be some ferromagnetic impurity present. The extrapolated (infinite H) molar susceptibilities are 0 ± 5 and 30 ± 10 erg-gauss^{-2}-mole^{-1} (or e.m.u.) at 299 and 78°K, respectively.

The paramagnetic and diamagnetic contributions are thus nearly equal, and any value quoted for χ_p will depend largely on what is assumed for the diamagnetic susceptibilities of the ions. The latter can only be estimated. Assuming Selwood's values are correct, χ_p is 125 ± 5 at 299°K and 155 ± 10 at

78°K.

The magnitude of the susceptibility plus the fact that it does not vary much with temperature is indicative of the presence of the Pauli paramagnetism characteristic of metals and the absence of permanent magnetic moments. Pauli paramagnetism is associated with the relative shift, in energy, of the metallic conduction bands (one for each spin orientation) produced by the magnetic field. The net result is the appearance of unpaired electrons as the populations of the two bands become unequal. These electrons can then contribute their spin moments to augment the applied magnetic field.

To a first approximation, the paramagnetic susceptibility due to these electrons is given by the simple relation

$$\chi_e = \beta^2 n(E_f) \tag{5}$$

where $n(E_f)$ is the total density of states (both conduction bands at the Fermi energy, E_f. If the density of states were known as a function of energy, it would be possible to calculate the number of electrons per atom in the metallic conduction band. The best that can be done, however, is to use the free electron model as a basis for calculations. The assumptions which shall be made are:

1. That there is a conduction band which is composed only of "d" states. While 's' states may be present, these are usually considered to form a wider band

which results in a lower density of states. Hence these states will be neglected.

2. That not all the "d" states may enter into the band structure. In other words, crystalline field effects may lift the degeneracy of the "d" states and then the band will be composed of only the lower states.

3. That the density of states is given by Eqn. 6

$$n(E) = \frac{D}{2\pi^2} \left(\frac{2m_e}{\hbar^2}\right)^{3/2} E^{1/2} \tag{6}$$

where D is the number of atomic "d" states contributing to the band, i.e., the degeneracy. The other symbols have their usual meanings.

4. That the density of LaI_2 is 6 gm-cm^{-3}. Compressed powders have densities of about 5.4-5.5 gm-cm^{-3} so the above estimate can not be too much in error.

5. That each La atom contributes one electron to the conduction band.

First the density of states is integrated over the energy (assuming T = 0°K), and the result is equated with the free electron concentration, N. The latter is estimated from assumptions 4 and 5. The result is an expression of the Fermi energy as a function of N and D. Substitution into Eqn. 6 yields the density of states at the Fermi level (Eqn. 7).

$$E_f = \left(\frac{3\pi^2 N}{D}\right)^{2/3} \frac{\hbar^2}{2m_e} \tag{7}$$

The substitution of this quantity into Eqn. 5 and the intro-
duction of the numerical values of the constants yields Eqn.
8, an expression of the paramagnetic susceptibility of the
conduction band, in terms of the degeneracy D.

$$\chi_e = 30.3 \ D^{2/3} \ \text{e.m.u.} \tag{8}$$

Since the lanthanum ions are surrounded primarily by iodide
ions the resulting crystalline field would probably split the
"d" levels so that D is either 2 or 3. If D = 3 (an octa-
hedral field), $\chi_e = 63 \times 10^{-6}$ e.m.u. which is lower than the
observed value, although the right order of magnitude. How-
ever, there is a ready-made fudge factor available called the
'effective mass' of the electron. In other words, the
electrons act as if their mass were different from the true
value. This concept is useful in describing the effect of
the lattice and other internal forces upon the motion of the
electron. A general description of the effective mass
concepts and its consequences on the properties of solid is
presented by Kittel (38).

The calculated results will agree with the experimental
values when the effective mass, m*, is about 2.7 m_e. Such a
value appears quite reasonable in as much as the 'effective
mass' for La metal is 4.3 m_e. Of course, other combinations
of D and m* can also be used.

The above calculations show that the presence of a

metallic conduction band could readily account for the observed paramagnetism. However, the only certain conclusion that can be drawn from the measurements is that there are no permanent magnetic moments and consequently no localized unpaired electrons in LaI_2.

Another Reduced Lanthanum Iodide

Inadvertently magnetic susceptibility measurements were made in some material with an overall composition of $LaI_{2.66}$. When an x-ray powder pattern indicated the presence of only LaI_3 and $LaI_{2.4}$, the magnetic data was processed in order to learn the nature of the reduced La ions in $LaI_{2.4}$. The results are tabulated in Appendix C.

The material has a net paramagnetism which, after correction for the ionic diamagnetism, can be attributed to a hypothetical La^{2+} ion. The paramagnetic susceptibility was strongly field dependent, varying inversely with H^2. Such behavior can not be explained.

In Fig. 7 two plots are shown of the reciprocal molar paramagnetic susceptibilities as a function of temperature. The lower line is based on the measurements taken when H = ⌣8 kilogauss. To obtain the upper line, the calculated values (for temperatures where there was sufficient data) were plotted against H^{-2}, and an extrapolation was made to infinite field. Since all the extrapolation lines had similar slopes, parallel lines were also drawn through the solitary points. The upper
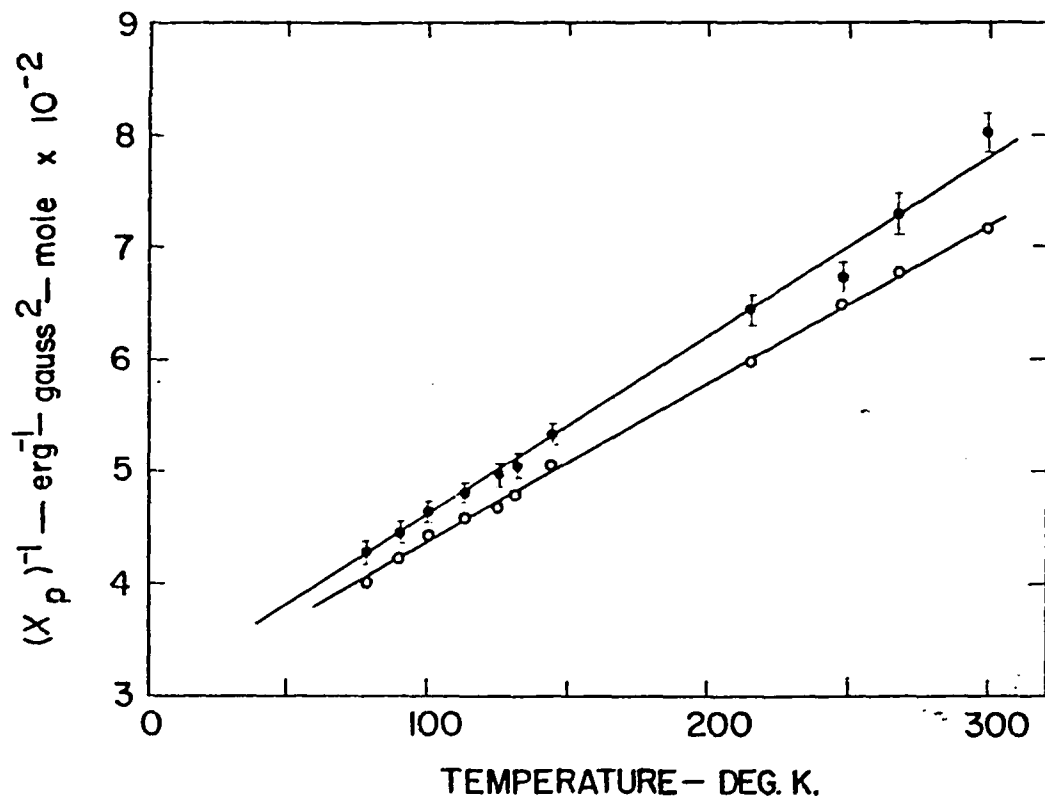
Fig. 7. Reciprocal paramagnetic susceptibility of the hypothetical La^{2+} cation. The open circles are the data for H = ~8 kilogauss, while the solid circles represent the extrapolated (infinite H) susceptibilities.

curve is a graph of these extrapolated susceptibilities.

The magnetic moments corresponding to the upper and lower lines are 2.3 and 2.4 B.M., respectively. Taken at face value the data would indicate that the La^{2+} ion has the $4f^1$ configuration of Ce^{3+} (μ = 2.54 B.M.) rather than $5d^1$ whose spin-only value is μ = 1.73 B.M. Since measurements were not made on a single phase (with a resulting loss of sensitivity) one is hesitant about making any definite conclusions.

The data do provide indications that in $LaI_{2.4}$ the extra electrons are localized on the cations rather than being spread over the whole lattice.

CONDUCTIVITIES OF THE PrI_3+Pr AND NdI_3+Nd SOLUTIONS

The electrical conductivities of the pure triiodides were measured using a capillary cell which was made from MgO rather than from Al_2O_3 as used by Bredig and co-workers in the earlier studies of the MCl_3+M melts. The substitution was unintentional and only after the experiments had been completed was the error discovered.

Unfortunately the MgO cell was attacked by the pure triiodides, presumably forming MgI_2 and Pr(Nd)OI. The measured conductivities are thus somewhat in error, although not primarily as the result of the altered composition but because the enlargement of the capillary changed the cell constant. The pure salts were remeasured later by Bredig, et al. (39), and their values are up to 5% lower than those reported here.

The use of the MgO cell had a further effect in that the MgI_2 introduced into the melt was subsequently reduced by the added rare earth metal. Thus the true compositions were less than those calculated from the weights of the added metal. All numerical data on the conductivities of these solutions can be found in Appendix D. In Fig. 8 the conductivities are shown as a function of composition. Also included are the more recent results obtained by Bredig (39) on the La, Ce and Pr solutions, as well as the earlier data for the chloride systems.
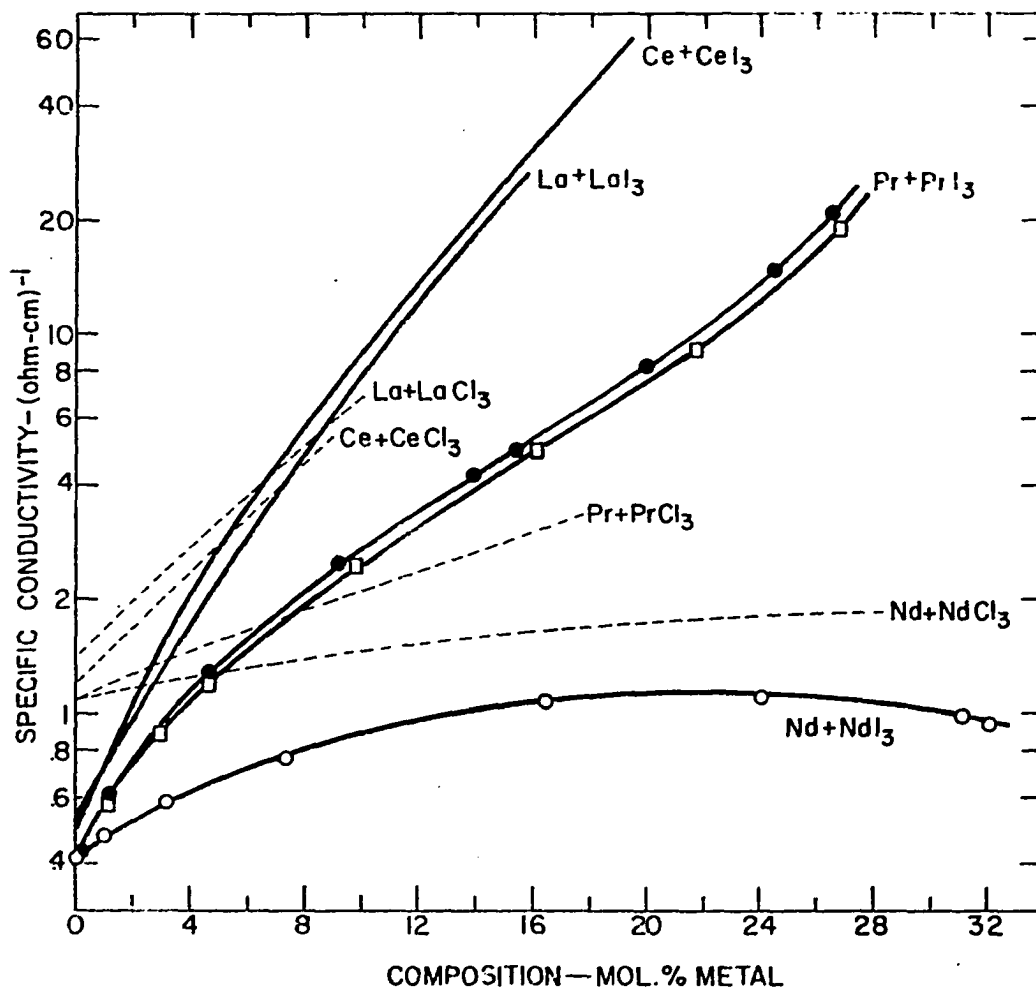
Fig. 8. Specific electrical conductivities of the metal-
metal halide solutions. The open figures (circle
or square) represent the data obtained in this
investigation. The solid circles are the data
obtained subsequently by Bredig (39) for the
Pr+PrI₃ melts. The conductivities of other
solutions are shown for comparison.

NdI_3+Nd Solutions

As in the $NdCl_3$+Nd solutions, the electrical conductiv-
ities of the NdI_3+Nd melts indicate that a charge transfer
occurs primarily through the movement of ions. Thus the
dissolution of Nd metal in either $NdCl_3$ or NdI_3 results in
the formation of the Nd^{2+} cation whose electron configuration
was just determined.

By extrapolating the data to 33.3 mole % Nd, the specific
conductivity of NdI_2 is estimated to be about 0.90 $(ohm-cm)^{-1}$
at 820°C. If some allowance is made for the Nd used in
reducing the MgI_2 impurity, then this estimate may drop to
about 0.85 $(ohm-cm)^{-1}$.

From the temperature dependence of the NdI_3 conductivity,
an activation energy of 6.1 $\pm$ 0.1 kcal/mole was calculated, in
good agreement with the data taken later by Bredig [39] with
the Al_2O_3 cell. The temperature dependence of a reduced
solution (32.1 mole % as calculated from the added metal) was
also measured and from this data the activation energy was
determined to be 6.3 $\pm$ 0.1 kcal/mole.

In the $NdCl_3$+Nd system positive deviations from an
additive conductivity relationship were observed which reached
their maximum near 16-17 mole % Nd metal. Bredig [20] suggest-
ed that this effect was the result of an electron transfer
mechanism between adjacent Nd^{3+} and Nd^{2+} ions. The rate of
this reaction would be proportional to x(1-x), where x is the

mole fraction of one species, as was observed. A similar
behavior is found in the NdI_3+Nd solutions but to a greater
degree. An actual decrease in conductivity was observed when
the composition approached NdI_2 whereas in the $NdCl_3+Nd$, the
conductivity only leveled off.

The proposed electron transfer reaction is very attrac-
tive and seems to be a logical concept. However, a note of
caution should be interjected. A conductivity maximum is also
observed in the $CaCl_2-MgCl_2$ system (40) where the existence of
an electron transfer process is very remote. Thus there may
be another interpretation since detailed explanations of the
deviations from additivity in many binary systems are not
well understood.

PrI_3+Pr Solutions

Fig. 8 shows clearly that the behavior of the PrI_3+Pr
system is intermediate to that exhibited by the corresponding
solutions of its neighboring elements. Of the two Pr curves,
the lower is derived from the present data while the upper is
that which was subsequently determined by Bredig. At low
concentration the curves are diverging but remain displaced
from one another by a constant amount at the higher concentra-
tions. This can be explained if the reduction of the MgI_2
were a slow process, being complete only after several
additions of Pr metal had been made. The displacement (at
higher concentrations) is close to that calculated from the

weight loss of the MgO cell.

The conductivity of PrI_3 was measured only at two temperatures. The activation energy (6.2 kcal/mole) calculated from these data is similar to that of NdI_3, as expected. More importantly, the temperature dependence of a solution whose calculated composition was $PrI_{2.52}$ was also measured. The dependence was much lower than for PrI_3 although still positive. The corresponding activation energy was only 1.6 $\pm$ 0.4 kcal mole^{-1}. This suggests that as the I/Pr ratio decreases further, there may be a point at which the dependence would become negative, i.e., metal-like. The contrast with the Nd solution is evident.

RESISTIVITIES OF THE SOLID 'ELECTRONIC' DIIODIDES

The measurement of the resistivities of the 'electronic' diiodides required by far the greatest expenditure of time and effort but yielded the smallest return in tangible results. Pure specimens of CeI_2 and PrI_2 could not be made and, in desperation, measurements were attempted on the specimens as cast.

Unfortunately, the mechanical strength of these impure specimens was quite low. In order to obtain low, constant contact resistances ($\sim$1-2 ohms), pressure had to be exerted by the potential probes and the power leads. This necessary pressure generally introduced cracks and fissures that propagated readily; a phenomenon that was observed even with the stronger LaI_2 specimens. As the result, reliable data on the temperature dependence of the resistivities were obtained on only three specimens (two compounds). These data are presented in Fig. 9 and are also tabulated in Appendix E.

The lower curve in Fig. 9 (which refers to the right hand ordinate) describes the behavior of two LaI_2 specimens. In both samples the I/La ratio was 2.00 ± 0.01. In view of the experimental difficulties, the agreement is highly gratifying.

The resistivity of LaI_2 is approximately equal to that of La metal (ccp structure) at room temperature. This low value of the resistivity for LaI_2 and its slight paramagnetism which
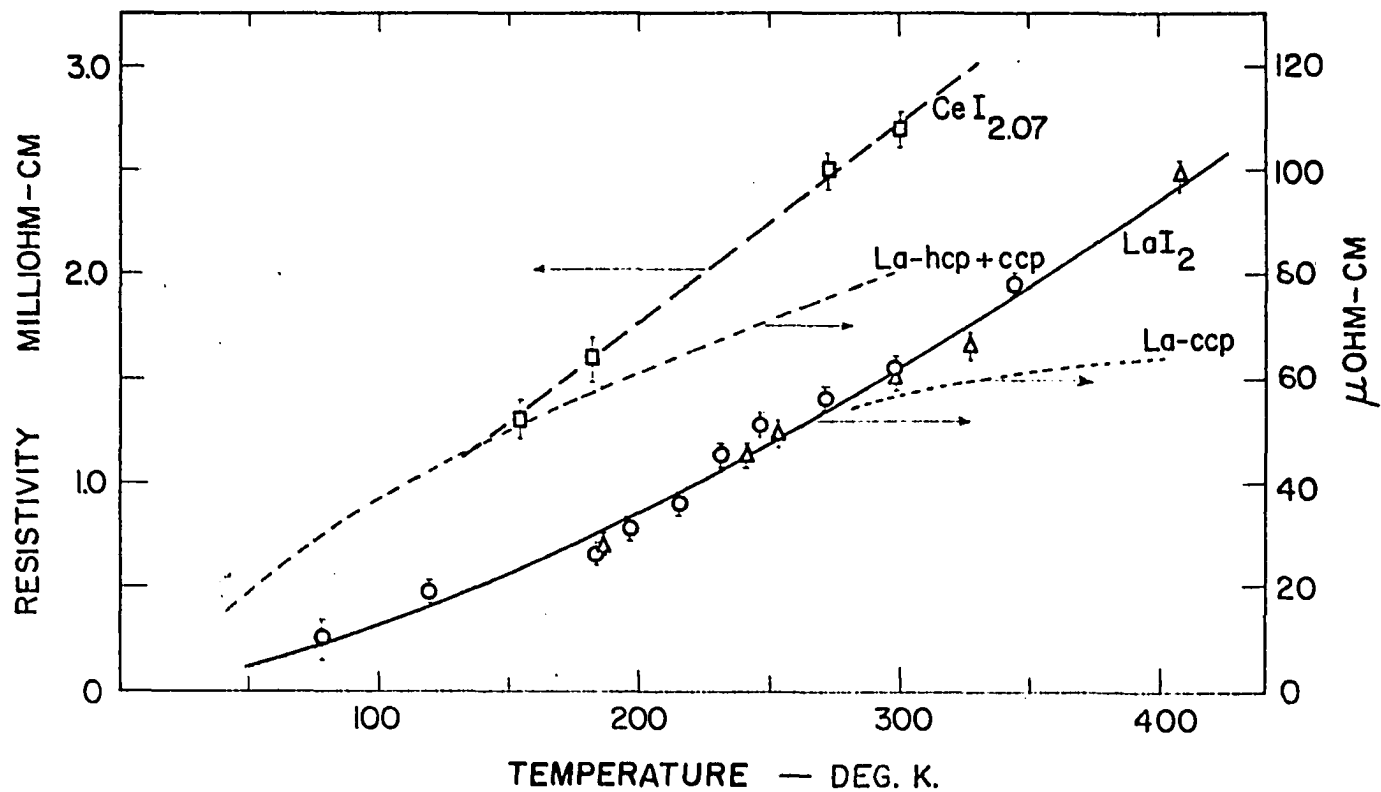
Fig. 9. The electrical resistivities of LaI₂ and CeI₂.₀₇. The data for the two LaI₂ specimens are separately marked by the circle and triangle. The resistivities of La metal are shown for comparison.

was discussed earlier provide good evidence that a truly metal-like conduction band is present.

Now a conduction band can be pictorially described as arising from the overlap of some atomic electron wave functions. To a first approximation the density of states at the Fermi level, and hence the resistivity, will vary inversely with the degree of overlap, i.e., the greater the overlap, the smaller the resistivity.

Note in Fig. 9 that while the LaI_2 resistivity is roughly proportional to temperature, the curve is concave upwards. This curvature may be the result of a large temperature coefficient of expansion which reduces the overlap of the electron wave functions.

The existence of a large coefficient of expansion was inferred from the low temperature behavior of the samples. Although a firm pressure was applied to the specimens when they were loaded into the sample holder, as the temperature was decreased a point would be reached where the probe leads either barely made electrical contact or became separated completely. The large relative error associated with the measurements at liquid nitrogen temperature was caused by this behavior for a slight jostling of the apparatus alternately made and broke electrical contact. When the specimens were allowed to warm up, good contacts were again restored. This large expansion coefficient may also account

for the inability to heat the specimens to temperatures greater than ~200°C without fracture occurring.

The contraction and expansion of the Lavite holder was ignored in the above discussion. The experimental behavior could also be explained if the holder expanded on cooling, but such a phenomenon would be very surprising.

The upper curve in Fig. 9 (left hand ordinate) shows the behavior of a specimen whose composition was $CeI_{2.07\pm0.01}$. Although the magnitude of the resistivity is much greater than LaI_2, the specimen still exhibits the positive temperature dependence that is characteristic of metals.

According to the phase diagram, the specimen was a mixture of CeI_2 and $CeI_{2.4}$, with the latter as the minor constituent. If the $CeI_{2.4}$ is presumed to have a large relative resistivity, its presence will serve to reduce the effective cross-sectional area of the specimen. Thus the true resistivity of CeI_2 may be much less, even comparable to that of LaI_2. In support of this view, room temperature resistance measurements on another specimen (composition $CeI_{2.04}$) yielded resistivities of about 300 ± 100 μ-ohm-cm. These measurements were obtained in an early experiment using D.C. circuitry, thus accounting for the large uncertainty.

Data for PrI_2 is even more sparse. The resistivity of one specimen ($PrI_{2.07}$) was measured at room temperature and found to be 350 μ-ohm-cm. Measurements were attempted at

another temperature but the specimen fractured.

The other specimen on which measurements were attempted had the nominal composition $PrI_{1.89}$ but was probably PrI_2 with an admixture of finely dispersed metal. Its resistivity at room temperature was initially 2.5 milliohm-cm. Measurements were also taken as the specimen was first cooled to 200°K and then heated to almost 600°K, but there is much doubt as to their validity. Because an insulating layer had formed at the specimen-power contact interface, applied voltages in excess of 2 volts were necessary to pass current. When this occurs the battery-powered preamplifier in the detector circuit does not have a linear response and, as a result, the calculated resistivities were in the range 0.5 to 0.8 milliohm-cm.

If the data are taken at face value there is a positive temperature dependence below 300°K and a negative dependence at higher temperatures. At first it was thought that the latter behavior might have been due to the annealing of the specimen since after the specimen had been cleaned and reset in the apparatus, the room temperature resistivity was only 1.5 milliohm-cm. However, the specimen was then heated slowly, with satisfactory electrical continuity, and the resistivity still dropped slightly to 1.4 and 1.3 milliohm-cm at 81° and 162°C, respectively.

The resistivities of these impure specimens do indicate that a considerable number of free or mobile electrons are

present in both CeI_2 and PrI_2. This fact, however, does not exclude the possibility that competing localized electron orbitals may also be present.

The A.C. resistivities of the specimens of all three compounds are frequency independent only below $\sim 10^3$ cps. The quoted values of course are those measured in the low frequency region. The resistivities are usually, but not invariably, greater at higher frequencies. The explanation for this is not known.

GENERAL DISCUSSION

The Solid Dihalides

In the preparation of these solid dihalides, the normal trivalent cation has nominally been reduced to the divalent state; each metal ion acquiring the rights to one additional electron. The experiments just described were designed to determine the disposition of that electron. (In the rest of this discussion, the noun electron will refer to the extra, added electron.)

In effect each cation was assumed to have the electron configuration of its normal tripositive state with the extra electron having its choice of the remaining vacant orbitals. In the dihalides of Nd, it was found that this electron went into a '4f' orbital. Thus it is localized on a particular ion, producing a conventional dipositive ion.

In LaI_2, on the other hand, the evidence shows this additional electron does not belong to any particular ion but that it has been delocalized into a metal-like conduction band where it is possessed by the crystal as a whole. From what atomic states is the conduction band derived? In the experimental discussion, the calculations implied that the '5d' orbitals were the source, although the reasons for this choice were not given fully. A more complete justification will now be attempted.

There are three types of orbitals that can be considered,

the '4f', '5d', and '6s'. The '6p' orbitals are generally
thought to be too high energetically to be pertinent to this
discussion. Of the three, the '4f' orbitals lie deep in the
potential field of the nucleus and their radial extension is
too small to give an effective overlap with similar orbitals
of the neighboring cations. Thus the choice is between the
'6s' and '5d' orbitals. In either of these, the extra
electron would have a large extension into the surrounding
space, with the '6s' orbital probably being the more diffuse.
There is spectral evidence (41) that in the ground state of
of the gaseous La^{2+} ion, the electron is in a '5d' orbital
rather than the '6s'. The same study infers that the '4f'
orbitals are the next lowest in energy since the '5d'-'4f'
transitions were presumed to be in the infra-red portion of
the spectrum. This location implys that the '4f' levels lie
about 1 ev higher in energy than the '5d'.

Now in the solid LaI_2, the juxtaposition of the iodide
anions near the rare earth metal cation should perturb the
'5d' orbitals and increase their energy although affecting the
'4f' orbitals relatively little. However, the '5d' orbitals
do not respond equally to the anion environment. Those
orbitals which tend to avoid the nearby anions will have
lower energies. Hence it is conceivable that, in certain
anion configurations, one or more of the '5d' orbitals can
still be the lowest available energy levels.

It seems significant that in the other 'metallic' compounds of the rare earth elements the anionic environment of the cation is quite different from that in the normal salts. The normal trivalent cation presents an approximately spherical electron density surface, the angular dependence due to the partially filled 'f' shell being somewhat buried beneath the filled outer shells. As a result the predominant crystalline forces appear to be of a van der Waals or electrostatic nature with the largest possible number of anions surrounding the cation. Depending on the size of the anion, the coordination number varies between eleven in the case of the trifluorides to as low as eight (almost nine) in the triiodides. In contrast, there are only six anion nearest neighbors in an octahedral or a tetragonally distorted arrangement in the MS and MC_2 compounds.

A possible explanation may be that when the coordination number is large, the anions act effectively as a spherical perturbing potential with the result that the various 'd' states are not differentiated, all having a relatively high energy. Therefore, only with a smaller number of anion neighbors can the symmetry properties of the 'd' states be exploited in generating lower energy levels.

While the structure of LaI_2 is not known, the x-ray powder pattern can tentatively be indexed on a tetragonal basis. This suggests that there may be an octahedral

arrangement of iodide ions around the La cation here also.

From the contrasting properties of LaI_2 and $NdI_{1.95}$ the idea naturally develops that there is a shift of an 'F' state downward in energy relative to a 'D' state as the lanthanide series is traversed. (The designations 'F' and 'D' denote whether the electron goes into a localized 'f' orbital or into a 'd' orbital which may or may not be combined with other 'd' orbitals into a conduction band.) The use of Slater's (42) rules for the estimation of electron energies provides a basis for this idea. For the hypothetical M^{2+} gaseous ions of the series La through Nd, placing the electron in the '4f' orbital initially yields a smaller amount of energy than when the site is a '5d' orbital. But the difference in energy decreases as the series is traversed until at Nd the occupancy of a vacant '4f' produces more energy. The above calculations are at best rather approximate, but the results are put on a firmer basis by a recent partial analysis of the M^{2+} spectra (43). The '4f'-'5d' transitions, while not observed for La^{2+}, were found for Pr^{2+}. The ground state of Pr^{2+} is the '4f³' level $^4I_{9/2}$ which lies about 11,000 cm^{-1} (1.36 ev) below the lowest level of the '4f²5d' configuration. These transitions were also observed in the Yb^{2+} spectra where the 'F' state is now some 4.3 ev below the 'D' state.

Thus attention is directed to the diiodides of the intervening elements where there may be a competition between

energy states for the electron. The resistance measurements
only show that some relatively free electrons are present in
both CeI_2 and PrI_2. How would the presence of competing
energy states affect the resistivity? Qualitatively, the
resistivity would be expected to increase significantly since
the localized states would act as trapping and scattering
sites. An analogous behavior is seen when the resistivities
of the transition metals are compared to those of the alkali
metals. Here the greater density of states of the 'd' band
provides the scattering and trapping sites, while contributing
relatively little to the overall conduction process.

The lowest measured resistivities of CeI_2 and PrI_2 were
about six times that of LaI_2. However, both compounds were
heavily contaminated by other phases and the true values are
no doubt lower. Thus the presence of competing localized
states is an unresolved point.

The x-ray powder patterns for these two compounds could
provide a very slight basis for deciding whether any 'F'
states are present. Both CeI_2 and PrI_2 were reported to be
isostructural with LaI_2 (23) but further scrutiny indicates
that in PrI_2 the symmetry has seemingly shifted from tetragon-
al to orthorhombic. If this distortion were caused by the
presence of 'F' states, then such states would be expected to
be absent in CeI_2, the electron going solely into a 'D' band.

The logical way to detect the presence of such 'F' states

would lie in the measurement of the magnetic susceptibilities. While a practical method for CeI_2, this would be rather futile for PrI_2 since the moments for Pr^{3+} and $Pr^{2+}(=Nd^{3+})$ are very similar; 3.62 and 3.68 B.M., respectively.

It is curious that other electrically conducting dihalides are not formed. At first thought, it might seem that the anions must participate in the construction of the conduction band, using some vacant higher energy levels, with only the iodide ions having such levels at a sufficiently low energy. This writer disagrees with this view, believing that there is only an indirect effect.

In support, certain semiconductor properties can be quoted (44). In those semiconductors where the crystal lattice can be split into two sublattices, one of "positively" charged atoms and one of "negatively" charged atoms, it is found that the mobility of electrons depends directly only on the positive sublattice. For instance partial substitution of Sb for Bi in Bi_2Se_3 reduces the electron mobility in a manner analogous to the alloying of metals while a similar substitution of Te into the negatively charged Se sublattice does not alter this mobility. Thus the electron avoids any negatively charged constituent of the crystals in semiconductors and there is no reason to believe this behavior will change in the metal-like compounds where the electronegativity difference of the component atoms is even greater.

An indirect effect may be based on the polarizibility of the halide anion. In those anions which are more polarizible, the outer electron density can distort to avoid the cation orbitals which then will be lower in energy and overlap more. This increase in overlap implies a lower resistivity. An example may be the thallium(I) halides (45) which under high pressure become metallic. The resistivities drop by a factor of 100 each time the anions are changed from Cl^- to Br^- to I^- in spite of the greater Tl-Tl separation.

The Metal-Salt Solutions

The concept of competing 'F' and 'D' states should also be useful to the explanation of the electrical properties of the metal-salt solutions. In the later part of this section, the implications of this hypothesis will be explored, but first an earlier explanation will be reviewed and discussed.

It is apparent from the observed conductivities that a successful description of the solute species can not be made in terms of a single entity. Bredig (20) has suggested that there is an equilibrium between a M^{2+} cation and an electron whose physical description is somewhat vague but which

$$M^{2+} \rightleftharpoons M^{3+} + (e)^-$$
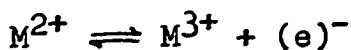
henceforth shall be termed an electronide ion. In order to be consistent with the cryoscopic data of the dilute solutions these electronide ions must behave as anions, thus their

resemblance to the F centers of solids. The electronic part of the total conductivity is attributed to these electronide ions, which are considered to be relatively mobile. Presumably, as the metal concentration increases, these electronide ions interact and ultimately form a metallic conduction band. By shifting the proposed equilibrium gradually from right to left, the conductivity behavior of the four rare earth metals in solution can be explained.

The electronide concept is very useful in describing certain phenomena in solids but is defined there on the basis of a rigid, regular crystal structure which is stable for long times. While there is an average short range order in the liquid, the actual ionic environment fluctuates considerably and the definition of the electronide ion becomes much less precise. The disorder and motion of the liquid, though, does provide a means for the mobility of such electrons.

In very dilute solutions, there is no a *priori* reason for discounting this theory, but as the solutions become more concentrated, doubts begin to arise. First, while there are examples in solids where a lattice can persist in spite of great numbers of vacancies, notably TiO (46), one would expect that in the liquid, a collapse to some other structure would soon occur. Second, one would expect strong electronide-electronide interactions as soon as such ions became near neighbors to one another. However, the recent measurements on

the LaI_3+La (39) solutions seem to dispute this. In a moderately concentrated solution (about 8 mole%), the overall conductivity has only increased about ten-fold and more importantly, its relative temperature coefficient (dlnK/dT) has not changed significantly from that of pure salt. At this concentration, every twelfth anion would be an electronide ion; thus each such ion would have on the average another electronide ion as one of its nearest anion neighbors.

In view of the results obtained on the solids, it is suggested that the above equilibrium be replaced by a competition between two kinds of dipositive solutes distinguished only by whether the extra electron is in an 'F' or a 'D' state. The former behaves as a true divalent cation, contributing only to the ionic conductivity while the latter is envisioned to be responsible for the electronic portion of the total conductivity.

In the La melts, the 'D' state is presumed the lower in energy while in the Nd solutions the converse is true. The question arises as to mechanism of the electronic conductivity and its relationship to the 'D' state. This will be discussed in later paragraphs after a discussion of some aspects of extrinsic semiconductors and their possible extension to these metal-salt melts.

The electric conductivity in many solid extrinsic semiconductors is due to electrons being excited from impurity

donor levels to the vacant conduction band of the host
lattice. When excited to this essentially empty band, the
electron moves freely through the host lattice and, while
being scattered the aperiodicity of the potential, it persists
in the upper band until trapped by another vacant donor level.
Consequently its mobility is relatively large; only a small
number of electrons being involved in the conduction process
at any one time. The important point is that the electron
can be trapped only by the relatively small number of vacant
donor sites (or at some other lattice imperfections).

The concept of band structure can be qualitatively
carried over into the liquid phase; the band edges becoming
diffuse from the lack of long range order (42). It is
tempting to consider the dilute metal solutions from this
viewpoint, but there is one great difference. In this picture
the donor site from which the electron is ionized is assumed
to be the 'D' state cation. After ionization, however, the
donor site becomes no different than any other solvent cation.
Conversely, every solvent cation is potentially a trap for the
ionized electron. The mobility must therefore be relatively
low and the conduction process can more conveniently be
described on an atomistic basis.

Consider the proposed solute in the dilute LaI_3+La
solutions, i.e., the 'D' state La^{2+} ion. The electron is at
the outermost edge of the cation and its energy is affected

very much by the potential field of the surrounding anions, depending markedly on their arrangement and distance. Clearly the random, thermal motion of the anions could be expected to raise the potential energy of this electron at times to quite high values. There are two ways in which the resulting 'stress' can be relieved. First, the electron may jump to another nearby M^{3+} cation where the energy of the vacant 'D' state is less. Second, the electron may take temporary refuge in the 'F' state provided that this level is available energetically.

The electronic conductivity may be explained by the first mechanism; the effect of an electric field giving slight statistically preferred direction to the transfers. This mechanism also explains why the relative temperature tempendence of the ionic and electronic conductivities have similar magnitudes. Both processes are closely related to the motion of the anions.

The picture that develops is one in which the electron is localized on a cation, its energy oscillating about some average value as the anion environment changes. Then at times the anion arrangement becomes particularly unfavorable and the electron jumps to another nearby cation. To put it another way, the thermal motion supplies that energy needed to overcome a potential barrier between cations.

This picture is very similar to that depicted by Rice

(47) who proposed that the electronic conductance of a metal-salt solution arises from a random walk of the electron along the solute and solvent cations.

An electron mobility can be calculated by assuming that every 'D' state electron contributes to the electronic conductivity using Eqn. 9

$$K = ne\mu \qquad (9)$$

where μ is the mobility and (ne) is the electron concentration in coulombs/cm^3. For the La and Ce solutions the values range between 0.01 and 0.4 cm^2 V^{-1} sec^{-1}, gradually increasing with concentration. For electronic processes, these are low values but are comparable to those found in semiconductors such as non-stoichiometric NiO and Fe_2O_3.

These compounds are similar to the metal-salt solutions in that the mobility of the electrons is strongly temperature dependent, increasing exponentially with temperature, while in semiconductors such as Si and Ge where the mobility is large, a gradual decrease is observed when the temperature increases. The mechanics of electron transfer in these oxides has also been pictured as jump from one cation site to another over or through an intervening energy barrier.

The close similarity of the conductivities of the La and Ce solutions as a function of concentration (see Fig. 8) indicates that, irrespective of the assumed solute model, both

metals dissolve to give similar species. The interpretation here is that 'D' state M^{2+} ions are formed. On the other hand the dissolution of Pr yields a solute species with different properties. Using the concept of competing states, its conductivity behavior is interpreted as the result of both 'D' and 'F' state solute ions being present. In other words, the 'D' and 'F' states have similar energies in the Pr^{2+} ion and both states are partially occupied, thereby reducing the number of displaceable electrons.

There is a little sidelight that may be interesting. A semi-log plot of the data (as in Fig. 8) shows a feature which would be hidden on a linear graph. If it is granted that the slope of the conductivity-concentration curve is a characteristic of the solute produced, then the Pr results show an unusual behavior. In the PrI_3+Pr solutions the initial slope resembles that of the La and Ce solutions, but with deviations occurring as soon as a few mole per cent metal has been added. One wonders if this means that the first few additions of Pr metal produces primarily what is termed the 'D' state cation. The $PrCl_3$+Pr solutions do not show this behavior, resembling the Nd melts more closely.

The inference is that the 'D' is slightly lower in energy than the 'F' states in the iodide melts while the converse is true in the chloride solutions. As said before this is an interesting feature but any conclusion is pure speculation.

In the Nd solutions there seems to be no doubt but that
the solute species is the divalent 'F' state cation as in the
solid dihalides. There are positive deviations from an addi-
tive relationship of the ionic conductivities of the pure
salts when the nominal metal concentration is varied. As
mentioned earlier, Bredig (20) has suggested that this may be
the result of an electron transfer process from a M^{2+} cation
to an adjacent M^{3+} cation.

Let this process be presumed to be the correct explana-
tion. In other compounds where such processes are postulated,
it is the outer 'd' electrons which move about. Thus the
process can be described in terms of overlapping orbitals or
some similar picture. The transfer mechanism is vague in the
Nd case since the electron which is transferred is usually
considered to be largely shielded from external influences and
to have a small radial extension.

From the competing states hypothesis there is a 'D' state
which in Nd^{2+} may not be too much higher in energy above the
'F' state. (The magnetic susceptibility data implies that
the energy separation is greater than about 0.25 ev.) If
promotion to this state could occur, then a transfer to some
nearby M^{3+} cation becomes feasible. The electron transfer is
thus facilitated by a low lying excited 'D' state. This pic-
ture presumes then that the mechanism is similar to that
responsible for the electronic conductivity of the other rare

earth metal-salt solutions. If this picture is correct, then the $SmCl_2$-$SmCl_3$ melts should show less deviation from an additive relation.

One final comment, a physical description of the electron transfer process becomes uncertain and vague as the electron mobility increases. This is a reflection of our inability to make satisfactory definitions of solute and solvent when the electron is partially delocalized.

Future Experiments

In the earlier portions of this section, the conclusions drawn from the experiments on the solid dihalides were extended and extrapolated to explain the conductivities of the metal-salt melts. The hypothesis which developed, that of competing 'D' and 'F' electron states, appears to explain the data, but in the absence of additional evidence, it must be regarded as speculation. In the next pages, some experiments will be suggested that may provide the required confirmation.

First, the crystal structure of LaI_2 should be elucidated. A knowledge of the anion configuration about the La cation could provide supporting evidence that the metal-like conduction band must be composed primarily of such 'd' states as the d_{xy}, d_{yz}, and d_{xz}.

Second, the true resistivities of the pure compounds CeI_2 and PrI_2 should be determined, if possible, and the data for LaI_2 extended. Such data would provide indications whether

competing localized energy states are present. If all of
these compounds have nearly identical resistivities, then
such states would be deemed absent.

For their determination, it is suggested that an
electrode-less technique be used in order to eliminate the
difficulties caused by the relative large coefficient of
expansion of these materials as well as those caused by the
tendency for surface layers with peculiar electrical proper-
ties to form. Such a technique might be the calculation of
the resistivity from the change in inductance of a coil pro-
duced by the insertion of the diiodide specimen, as described
in a recent publication (48).

Third, measurement of the Hall coefficients of the
'metallic' diiodides could also supply evidence for the
possible presence of 'F' states. Where an appreciable amount
of such states are occupied, the Hall coefficient would have
a larger value due to the smaller number of mobile electrons.
This assumes that the conduction band has a density of states
curve which increases monotonically with energy. This
assumption is probably true since almost any band that might
be constructed would be half full or less.

Fourth, a detailed examination of the conductivities of
the molten metal-salt solutions as a function of temperature
as well as concentration could provide an illuminating insight
into the conduction processes. The more concentrated

solutions of La and Ce in their respective triiodides should also be explored; possible differences in dissolution modes may be observed.

Fifth, the intermediate iodide compounds should be investigated. The data on $LaI_{2.4}$, gathered accidentally, indicates that there are localized electrons in this compound and their electronic state should be accurately determined. The present data, although favoring the 'F' state La^{2+} cation, can not be considered definitive.

In the reduced rare earth metal compounds, except with La, the study of the reduced cations is complicated by the properties of the normal tripositive cation. For instance, any study of the Pauli paramagnetism of CeI_2 must be carried out in the shadow of the large paramagnetism of the Ce^{3+} ion. Thus considerable ingenuity will be necessary to detect the desired properties.

Many of the properties that one wishes to observe depend on the characteristics of the M^{2+} ion in a particular anion environment and significant evidence could be gathered if this anion environment were preserved while eliminating the normal M^{3+} ion. Now Dieke (49-52) has published a series of papers investigating the spectra of some rare earth metal cations in a dilute solid solution in $LaCl_3$, essentially isolating the cations while at the same time preserving the anion environment.

It is proposed that this technique be used for the study of the divalent rare earth metal cations. The solid solvents could be the strontium halides, although the stability of the Sr^{2+} cation with respect to M^{2+} must be determined. The size of the Sr^{2+} ion is comparable with the estimated sizes of the M^{2+} ions and in addition the anion environment might be similar. The crystal structures of $SrBr_2$ and $NdI_{1.95}$ are identical (15), based on their x-ray powder patterns. If such solid solutions were stable, then spectral and magnetic studies could pinpoint the electronic states of the M^{2+} ions and prove rather conclusively whether the concept of competing states is or is not a valid hypothesis.

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APPENDIX A

Magnetic Susceptibilities of Nd Trihalides

Table 1. $NdCl_3{}^a$

Δw gm.	H^2 kilogauss^2	T deg. K	χ_M $\dfrac{erg}{gauss^2\ mole}$	$(\chi_p)^{-1}$ $\dfrac{gauss^2\ mole}{erg}$
0.307	63.58	300	0.005322	184.5
0.2414	49.73	300	0.005350	183.5
0.1448	29.64	300	0.005384	182.4
0.0759	15.60	300	0.005363	183.1
0.0490	10.00	300	0.005401	181.9
0.420	29.41	77	0.01574	63.1
0.342	29.41	109	0.01282	77.4
0.296	29.41	126	0.01109	89.4
0.2520	29.41	159	0.009444	104.8
0.2138	29.41	195	0.008013	123.3
0.2085	29.41	198	0.007814	126.4
0.1937	29.41	220	0.007259	137.8
0.1729	29.41	247	0.006480	152.0
0.1714	57.14	491	0.003306	293.8
0.1740	57.12	479	0.003358	289.4
0.1794	57.12	466	0.003462	280.9
0.1912	57.14	434	0.003688	264.1
0.2059	57.14	404	0.003968	245.9
0.2153	57.18	387	0.004150	235.4
0.2273	57.18	364	0.004380	223.3
0.2449	57.18	335	0.004721	207.5
0.4794	34.12	78	0.01549	64.2
0.4786	34.12	78	0.01546	64.3
0.4702	34.12	80	0.01519	65.4
0.4630	34.12	81	0.01496	66.4
0.4267	34.12	92	0.01388	71.5
0.3093	34.12	149	0.00999	99.1
0.2823	34.12	167	0.00912	108.5

χ_d ^{a}w = 11.32 gm.; h = 25.39 cm.; M = 250.64; χ_d = .000098 erg gauss^{-2} mole^{-1}.

Table 2. NdI_3[a]

Δw gm.	H^2 kilogauss^2	T deg. K	χ_M $\dfrac{erg}{gauss^2\ mole}$	$(\chi_p)^{-1}$ $\dfrac{gauss^2\ mole}{erg}$
0.3234	62.00	300	0.005456	177.6
0.2541	48.59	300	0.005470	177.1
0.1734	33.21	300	0.005461	177.4
0.1049	20.03	300	0.005478	176.9
0.0609	11.26	300	0.005657	171.4
0.5122	29.80	78	0.01798	55.1
0.4616	29.80	89	0.01620	61.1
0.4381	29.80	92	0.01538	64.3
0.3537	29.80	134	0.01242	79.4
0.3317	29.80	139	0.01165	84.6
0.3117	29.80	148	0.01094	90.0
0.2802	29.80	166	0.009835	99.9
0.2447	29.80	192	0.008589	114.1
0.2229	29.80	211	0.007824	125.0
0.2051	29.80	229	0.007199	135.6
0.1856	29.80	251	0.006515	149.5
0.1741	53.74	479	0.003565	280.5
0.1823	53.61	451	0.003733	267.9
0.1934	53.61	428	0.003949	253.2
0.1925	53.60	431	0.003933	254.3
0.2161	53.60	379	0.004393	227.6
0.2335	53.60	351	0.004733	211.3
0.2514	53.60	328	0.004082	196.8
0.2636	53.60	314	0.005320	188.0

[a] $w = 21.39$ gm.; $h = 21.74$ cm.; $M = 525.0$; $\chi_d = .000176$ erg gauss^{-2} mole^{-1}.

APPENDIX B

Magnetic Susceptibility of Nd Dihalides

Table 3. $NdI_{1.95}$[a]

Δw gm.	H^2 kilogauss^2	T deg. K	χ_M erg gauss^2 mole	$(\chi_p)^{-1}$ gauss^2 mole erg
0.4152	73.89	297	0.003597	268.5
0.3784	73.89	334	0.003278	293.7
0.3737	73.89	338	0.003238	297.2
0.3714	73.89	340	0.003218	299.0
0.3690	73.89	343	0.003197	300.8
0.3664	73.89	347	0.003174	302.9
0.3638	73.89	351	0.003152	305.0
0.2522	73.70	595	0.002191	431.4
0.2545	73.70	582	0.002211	427.7
0.2576	73.70	569	0.002238	422.8
0.2612	73.70	554	0.002269	417.4
0.2687	73.70	525	0.002334	406.3
0.2725	73.70	516	0.002367	401.0
0.2756	73.70	507	0.002394	396.7
0.2771	73.70	503	0.002407	394.6
0.2800	73.70	495	0.002432	390.8
0.2847	73.70	483	0.002473	384.6
0.2889	73.70	471	0.002509	379.4
0.2920	73.70	464	0.002536	375.5
0.2958	73.70	454	0.002569	370.9
0.2999	73.70	445	0.002605	366.0
0.3042	73.70	436	0.002642	361.1
0.3098	73.70	425	0.002691	354.9
0.3178	73.70	410	0.002760	346.4
0.3254	73.70	399	0.002826	338.6
0.3320	73.70	388	0.002884	372.1
0.3382	73.70	377	0.002938	326.3
0.3448	73.70	368	0.002995	320.3
0.3590	73.70	361	0.003118	308.2
0.3463	74.00	368	0.002995	320.3

[a] w = 27.99 gm.; h = 23.35 cm.; M = 391.74 gm. mole^{-1}; χ_d = .000127 erg gauss^{-2} mole^{-1}.

Table 3. (Continued)

Δw gm.	H^2 kilogauss^2	T deg. K	χ_M $\dfrac{erg}{gauss^2\ mole}$	$(\chi_p)^{-1}$ $\dfrac{gauss^2\ mole}{erg}$
0.3596	74.00	353	0.003111	308.8
0.3668	74.00	346	0.003173	303.0
0.3671	74.00	344	0.003176	302.8
0.3745	74.00	335	0.003240	397.0
0.3834	74.00	327	0.003317	290.4
0.3938	74.00	316	0.003407	283.0
0.5535	66.34	195	0.005341	182.9
0.2595	30.98	195	0.005361	182.3
0.1363	16.09	195	0.005424	179.2
1.265	63.66	79	0.01272	77.8
0.6063	30.65	79	0.01266	78.2
0.3131	15.92	79	0.01262	79.2
0.2086	10.41	79	0.01283	77.2
0.3798	66.55	298	0.003653	264.6
0.1777	31.01	298	0.003668	263.5

Table 4. $NdI_{1.95}$ continued[a]

Δw gm.	H^2 kilogauss^2	T deg. K	χ_M $\dfrac{erg}{gauss^2\ mole}$	$(\chi_p)^{-1}$ $\dfrac{gauss^2\ mole}{erg}$
0.335	58.46	301	0.003554	271.7
0.323	58.46	314	0.003426	281.6
0.292	58.46	353	0.003098	310.1
0.2811	58.46	370	0.002982	321.6
0.2593	58.46	411	0.002751	347.5
0.2515	58.46	426	0.002668	357.8
0.2380	58.46	472	0.002525	377.1

[a] $w = 27.99$ gm.; $h = 22.62$ cm.; $M = 391.74$ gm. mole^{-1}; $\chi_d = .000127$ erg gauss^{-2} mole^{-1}.

Table 4. (Continued)

Δw gm.	H^2 kilogauss^2	T deg. K	χ_M erg gauss^2 mole	$(\chi_p)^{-1}$ gauss^2 mole erg
0.3110	63.49	356	0.003038	316.0
0.3154	63.49	351	0.003081	311.7
1.228	63.60	79	0.01197	82.6
0.947	48.99	79	0.01199	82.5
0.583	30.06	79	0.01203	82.3
0.367	19.00	79	0.01198	82.6
0.227	11.78	79	0.01195	82.8
0.167	8.72	79	0.01188	83.3
0.752	48.97	104	0.009523	103.6
0.693	48.97	114	0.008776	112.3
0.647	48.97	125	0.008194	120.2
0.509	48.97	152	0.006446	152.1
0.479	49.34	166	0.006021	162.7
0.445	49.34	184	0.005593	174.8
0.3929	49.34	213	0.004938	197.4
0.3389	49.34	245	0.004260	227.9
0.3443	49.34	240	0.004326	224.6
0.3142	49.34	268	0.003949	245.3
0.952	49.24	78	0.01199	82.5
0.924	49.24	87	0.01164	85.0
0.838	49.24	97	0.01055	93.6
0.746	49.24	108	0.009396	105.0
0.671	49.24	118	0.008451	116.6
0.683	49.24	113	0.008602	114.6
0.652	49.24	127	0.008212	119.9
0.607	49.24	140	0.007645	128.7
0.5027	49.24	156	0.006331	154.8
0.1781	15.06	146	0.007334	134.0
0.1648	15.06	154	0.006786	144.7
0.1456	15.06	176	0.005996	163.3
0.2878	50.04	301	0.003567	270.7

Table 5. $NdCl_{2.04}$[a]

Δw gm.	H^2 kilogauss^2	T deg. K	χ_M $\dfrac{erg}{gauss^2\ mole}$	$(\chi_p)^{-1}$ $\dfrac{gauss^2\ mole}{erg}$
0.3291	63.19	472	0.002542	382.0
0.3360	63.19	456	0.002595	374.5
0.3505	63.19	431	0.002706	359.6
0.3520	63.19	429	0.002718	358.0
0.3590	63.19	417	0.002772	351.2
0.3726	63.19	397	0.002877	338.8
0.3761	63.19	391	0.002904	335.7
0.3832	63.19	381	0.002959	329.6
0.3889	63.19	370	0.003003	324.9
0.4013	63.19	357	0.003099	315.1
0.4066	63.19	351	0.003140	311.0
0.4149	63.19	342	0.003204	304.9
0.4258	63.19	331	0.003288	297.4
0.4343	63.19	322	0.003354	291.6
0.4424	63.19	315	0.003416	286.5
0.3250	63.19	488	0.002510	386.8
0.3193	63.19	500	0.002466	393.5
0.3174	63.19	506	0.002451	395.9
0.3187	63.19	503	0.002461	394.3
0.3137	63.19	522	0.002422	399.9
0.3108	63.19	526	0.002400	404.0
0.5497[b]	66.52	299	0.003569	274.4
0.2568[b]	31.01	299	0.003576	273.9
0.4542[b]	16.06	78	0.01221	81.4
0.859 [b]	30.78	78	0.01205	82.5
0.3718[b]	31.06	195	0.005170	190.7
0.1936[b]	16.12	195	0.005262	190.0
0.413 [c]	50.01	301	0.003553	275.6
1.379 [c]	50.01	78	0.01186	83.8
0.384 [c]	13.55	78	0.01219	81.5
0.603 [c]	29.51	118	0.008774	113.0
0.3952[c]	29.57	122	0.005750	171.7
0.3317[c]	29.57	208	0.004826	204.0

[a] $w = 20.49$ gm.; $h = 23.35$ cm.; $M = 216.60$ gm. mole^{-1}; $\chi_d = .000075$ erg gauss^{-2} mole^{-1}.

[b] $h = 20.84$ cm.

[c] $h = 20.76$ cm.

APPENDIX C

Magnetic Susceptibilities of La Iodides

Table 6. $LaI_{2.03}$[a]

Δw gm.	H^2 kilogauss^2	T deg. K	χ_H $\dfrac{erg}{gauss^2\ mole}$
0.0020	64.6	299	0.000028
0.0020	55.4	299	0.000033
0.0016	32.9	299	0.000044
0.0012	19.1	299	0.000057
0.0009	11.6	299	0.000071
0.0066	64.2	78	0.000093
0.0057	51.7	78	0.000100
0.0041	29.7	78	0.000125
0.0030	18.5	78	0.000147
0.0022	11.6	78	0.000172

χ_d $^a w = 21.64$ gm.; $h = 25.53$ cm.; $M = 392.74$; $= -0.000124$ erg gauss^{-2} mole^{-1}.

Table 7. $LaI_{2.66}$[a]

Δw gm.	H^2 kilogauss^2	T deg. K	χ_M $\dfrac{erg}{gauss^2\ mole}$	$(\chi_p)^{-1}$ $\dfrac{gauss^2\ mole}{erg}$
0.0109	64.03	299	0.000308	718
0.0069	37.45	299	0.000332	---
0.0044	21.60	299	0.000368	---
			(0.000258)[b]	803

χ_d $^a w = 7.89$ gm.; $h = 20.37$ cm.; $M = 476$ gm mole^{-1}; $= -0.000158$ erg gauss^{-2} mole^{-1}.

[b]Extrapolated to infinite H.

Table 7. (Continued)

Δw gm.	H^2 kilogauss^2	T deg. K	χ_M $\dfrac{\text{erg}}{\text{gauss}^2\,\text{mole}}$	$(\chi_{p2})^{-1}$ $\dfrac{\text{gauss}^2\,\text{mole}}{\text{erg}}$
0.0232	62.33	78	0.000672	403
0.0144	37.97	78	0.000685	—
0.0087	21.57	78	0.000728	—
			(0.000622)[b]	—
0.0217	61.97	89	0.000632	429
0.0111	29.53	89	0.000685	423
0.0083	21.51	89	0.000728	—
			(0.000593)[b]	—
0.0206	62.17	100	0.000600	445
0.0109	30.69	100	0.000641	442
0.0078	21.51	100	0.000656	—
			(0.000560)[b]	—
0.0199	62.17	113	0.000578	466
0.0113	33.11	113	0.000616	454
0.0074	20.42	113	0.000656	—
			(0.000540)[b]	—
0.0192	64.03	131	0.000542	479
			(0.000504)[b]	477
0.0198	64.03	125	0.000558	505
			(0.000520)[b]	467
0.0181	64.60	144	0.000506	496
0.0102	34.07	144	0.000542	504
0.0069	21.61	144	0.000576	—
			(0.000468)[b]	—
0.0140	63.39	215	0.000399	534
			(0.000361)[b]	398
0.0125	63.39	248	0.000358	643
			(0.000340)[b]	649
0.0117	53.39	268	0.000334	672
			(0.000300)[b]	678
				729

APPENDIX D

Specific Conductivities of Metal-Salt Solutions

Table 8. PrI_3+Pr at 780°C

Composition mole % Pr	Sp. cond. $ohm^{-1} cm^{-1}$	Composition mole % Pr	Sp. cond. $ohm^{-1} cm^{-1}$
0.0	0.43	9.8	2.44
1.1	0.57	16.1	4.89
2.9	0.88	21.7	9.03
4.6	1.17	26.8	19.0

Table 9. NdI_3+Nd at 820°C

Composition mole % Pr	Sp. cond. $ohm^{-1} cm^{-1}$	Composition mole % Pr	Sp. cond. $ohm^{-1} cm^{-1}$
0.0	0.44	16.5	1.03
1.0	0.48	24.1	1.10
3.1	0.59	31.2	0.98
7.3	0.76	32.1	0.93

Table 10. Conductivities as a function of temperature

Solution	Temperature deg. C	Sp. cond. ohm^{-1} cm^{-1}
PrI_3	760	0.40
	780	0.43
16 mole % Pr in PrI_3	687	4.56
	739	4.66
	781	4.89
NdI_3	796	0.41
	822	0.44
	850	0.47
31.2 mole % Nd in NdI_3	643	0.55
	735	0.77
	819	0.98

APPENDIX E

Resistivities of the 'Electronic' Diiodides

Table 11. Resistivities at various temperatures

Compound	μ ohm cm	T deg. K	μ ohm cm	T deg. K
LaI_2, No. 1	10 ± 4	77 ± 1	45 ± 2	230 ± 1
	19 ± 2	118 ± 3	51 ± 2	246 ± 2
	26 ± 2	183 ± 1	56 ± 2	271 ± 1
	31 ± 2	195 ± 1	62 ± 2	298 ± 1
	36 ± 2	215 ± 1	78 ± 2	344 ± 1
LaI_2, No. 2	28 ± 2	186 ± 2	60 ± 2	298 ± 1
	45 ± 2	241 ± 2	66 ± 2	327 ± 1
	49 ± 2	253 ± 2	99 ± 4	408 ± 1
$CeI_{2.07}$	$(2.7\pm0.2)\times10^3$	300 ± 1	$(1.6\pm0.1)\times10^3$	181 ± 3
	$(2.5\pm0.2)\times10^3$	273 ± 1	$(1.3\pm0.1)\times10^3$	153 ± 10