1970

The synthesis and some physical properties of reduced scandium chloride, bromide, and iodide phases with unusual stoichiometries

Bill Crews McCollum
Iowa State University

Recommended Citation

McCollum, Bill Crews, "The synthesis and some physical properties of reduced scandium chloride, bromide, and iodide phases with unusual stoichiometries " (1970). *Retrospective Theses and Dissertations*. 4183.
https://lib.dr.iastate.edu/rtd/4183

70-18,892

McCOLLUM, Bill Crews, 1940-
THE SYNTHESIS AND SOME PHYSICAL PROPERTIES OF
REDUCED SCANDIUM CHLORIDE, BROMIDE, AND IODIDE
PHASES WITH UNUSUAL STOICHIOMETRIES.

Iowa State University, Ph.D., 1970
Chemistry, inorganic

University Microfilms, A XEROX Company, Ann Arbor, Michigan

THE SYNTHESIS AND SOME PHYSICAL PROPERTIES OF REDUCED SCANDIUM CHLORIDE, BROMIDE, AND IODIDE PHASES WITH UNUSUAL STOICHIOMETRIES

by

Bill Crews McCollum

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Inorganic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Ames, Iowa

1970

TABLE OF CONTENTS

	Page
INTRODUCTION	1
EXPERIMENTAL PROCEDURE	7
EXPERIMENTAL RESULTS AND DISCUSSION	25
FUTURE WORK	72
BIBLIOGRAPHY	76
ACKNOWLEDGMENTS	80
APPENDIX	81

INTRODUCTION

The present work stems indirectly from an interest in the solubility of metals in their molten salts. Though the solubility of metals in their molten salts is not a new topic, lack of sufficiently sophisticated methods of investigation, readily available and pure materials, and sometimes containers impervious to attack has made reliable work difficult until recently. A stimulus has been the availability of support spurred by long range interest in the technology necessary for the use of molten salts as solvents for fissionable materials or as a heat exchange medium in nuclear reactors. Thus, an increasing literature has resulted in the publication of several review articles (1-5) of which those by Corbett (4) and Bredig (5) are the most up to date and pertinent to the present topic.

The metal-molten salt systems of interest here are those in which metals are dissolved in their molten halides. Bredig has found it convenient to divide these solutions into two broad categories: those in which the solutions exhibit a partial metallic character and those in which a strong interaction between the metal and the salt occurs and the metal assumes a lower than normal oxidation state (5). From the accumulation of examples there seems to be no sharp dividing line between these categories. Solutions of the first sort are characterized by a high electronic conductivity. Typical examples are solutions of alkali metals in their halides. Solutions of the second sort, generally (but not always) have lower electronic conductivities and ionic conductivity represents a larger fraction of the total. The assumption of a lower than normal oxidation state by the metal in solution may lead to the crystallization of a stable solid "subhalide", and it is this possibility that is connected with the present work.

The systematic examination of the MX_3-M systems (where M is a rare earth metal and X is usually Cl or I) has been useful in comparing the stability of the various M^{2+} cations with respect to disproportionation. Corbett, Pollard, and Mee (6) have considered the extent of solubility of M in MCl_3 as a good indicator of the stability of M^{2+}. Considering the equilibrium,

$$2\ MCl_3(soln) + M(s) = 3\ MCl_2(soln)$$

the enthalpy of the equilibrium reduction is given by the Born-Haber cycle as

$$\Delta H^o_T = 3\ U_2 + \Delta H^o(\text{subl M}) + I_1 + I_2 - 2\ I_3 + -2\ U_3$$

where U_n is the enthalpy change for formation of pure liquid MX_n from gaseous M^{n+} and nX^-. The terms $3\ U_2 - 2\ U_3$ and I_3 (representing the "lattice" energies of the two liquid chlorides and the third ionization potential of the metal element) were presumed to vary smoothly across the lanthanide series, and the variation of the observed stabilities of M^{2+} (i.e., the variation of the solubility of M in MCl_3) was found to be chiefly related to variations of the heats of sublimation of the metals as reported by Habermann and Daane (7). Better, these stability variations were found to be reflected in variations of ΔG° (subl 1073) + I_1 + I_2 since U_2 and U_3 vary smoothly. Later, Johnson and Corbett (8) pointed out that variations in I_3 as estimated by Johnson (9) also show the irregularities exhibited by the enthalpies of sublimation for the metals. The variation in I_3 is energetically greater than for ΔH°(subl), and since I_3 is doubly weighted in treating the solution equilibrium above, it is seen to be the more important of the two. By a similar treatment of the disproportionation equilibria of the ionic rare earth diodides (or chlorides), the variation of the sublimation enthalpies of the metals and the third ionization potentials of the metals were shown to be of key importance to the stability of the solid dihalides (8).

The above treatment of the question of stabilities of solid dihalides depends on the applicability of the ionic model. In the rare earth iodide systems LaI_2, CeI_2, PrI_2 (10), and GdI_2(11) exist as metallic conductors while none of the same salt-like compounds should be stable to disproportionation. The relative stabilities of metallic iodides to disproportionation were also treated thermodynamically by Johnson and Corbett by a discussion of the equation

$$\Delta G_m^o = 3M - 2U_3 - (\Delta H^o(\text{subl}) + I_1 + I_2 + I_3) - T\Delta S_m^o$$

where M is the lattice enthalpy of the metallic salt. The free energies of formation of the metallic iodides were inferred to decrease smoothly across the rare earth system (except at Eu and Yb) becoming positive beyond gadolinium. By this approach, formation of metallic diiodides was considered independent of the stability of M^{2+}, except where a competition between stable ionic and metallic diiodides might occur (this does not happen in the rare earth series).

In considering the formation of a stable subhalide, an additional possibility is the formation of "non-Daltonian" compounds, here loosely meaning binary compounds the components of which are not related by small integers. Almost distressingly, compounds of this kind are also represented among the rare earth subhalides, examples being $LaI_{2.42}$ and $CeI_{2.4}$(10), $NdCl_{2.37}$ and $NdCl_{2.27}$(12), $GdCl_{1.6}$(11), $DyCl_{2.1}$ (13), and as many as nine phases appear to exist between $TmCl_{2.15}$ and $TmCl_{2.04}$(14). Further complicating matters, $GdCl_{1.6}$ may have substantial metal-metal interactions, and therefore is thought not to be related to the other examples given (15).

Scandium exhibits an exclusively trivalent aqueous chemistry, and is often thought of as a rare earth although it is the first of the 3d elements. Corbett and Ramsey (16) were led to investigate the $ScCl_3$-Sc system for reasons that the stability of the M^{2+} ion should increase from La^{2+} to Sc^{2+} and the prediction from Born-Haber cycle calculations by Barber, Linnett, and Taylor (17) that $ScCl_2$ should be on the borderline of stability. Before their work was complete, Polyachenok and Novikov (18) published phase results for the same system in which they reported the formation of stable $ScCl_2$. They no doubt had been led to investigate the system by their own prediction of stable $ScCl_2$ by Born-Haber cycle calculations (19). Corbett and Ramsey found no subchloride to exist and a very different liquidus curve and eutectic parameters. Since their $ScCl_3$ was almost certainly better (melting at 967° C. versus 953° C.) and Polyachenok and Novikov had container problems, it was concluded that the Russian work was in error.

A decision to investigate the ScI_3-Sc system, the chief topic of this dissertation, was based first on calculations using thermodynamic data tabulated by Nelson and Sharpe (20). From these, $ScCl_2$ and $ScBr_2$ should be unstable with respect to disproportionation and ScI_2 probably so with $\Delta G^\circ = -5 \pm 7$ kcal./mole. More important, the eutectic composition of 19 mole % Sc found by Ramsey and Corbett for the $ScCl_3$-Sc system was considered as good evidence that $ScCl_2$ was almost stable. Since the lattice energy of ionic ScI_3 should be somewhat less than for $ScCl_3$, this would tend to make the diiodide more stable with respect to disproportionation than the dichloride. Thus, it was thought that ScI_2 might be stable. If an ionic diiodide did not result, it was thought that a metallic diiodide might be stable since Sc^{2+} should have a $3d^1$ configuration analogous to the metallic rare earth diiodides where the presence of a d-electron is thought necessary to their existence. Another goal of the project was the investigation of some of the physical properties of any subiodide formed. The investigation of the $ScBr_3$-Sc system was to be considered only if the results on the iodide system seemed to warrant it.

From other scandium compounds there is no evidence for stable divalent scandium ion. The ScS (21) is metallic as is ScH_2 (22). A report of the preparation of ScO (23) from Sc_2O_3 and H_2 at high temperatures is suspect because of the stability of the hydride, and if ScO did exist, it probably would not contain discrete Sc^{2+} ions.

EXPERIMENTAL PROCEDURE

Preparation of the Anhydrous Metal Halides

The scandium metal used for the preparation of the trihalides was readily available in the Ames Laboratory in a high degree of purity. The following are typical impurity levels in p.p.m.: F, 250; O, 300; H, 10; Fe, 50; Si, < 20; Ca, < 30; Ta, 1500-2000; Y, 100; Er, < 100; Tm, Yb, Lu, < 70. The metal was used as turnings for convenience in dispensation except that metal chunks were used for equilibration experiments. Although scandium metal seems relatively inert to attack by air, some samples were observed to become somewhat tarnished after long exposure to air. Therefore, it was stored under vacuum except for the time required to weigh and transfer pieces to reaction containers.

Preparation of ScI_3

Scandium triiodide was prepared by a direct reaction of the elements. Although various designs of reaction containers have been used for metal-iodine reactions, it was found that a closed vertical tube of about 51 mm. o.d. fused silica was convenient. Scandium metal was held in a tungsten crucible which had been cleaned by induction heating under dynamic vacuum. The crucible was seated in an upper chamber of the reaction tube defined by a constriction in the fused silica container walls. Scandium metal and then iodine were introduced into the crucible via a short seven mm. o.d. fused silica tube topped by an 18/7 ball joint. This entrance tube was sealed under dynamic vacuum using a -195° C. cold trap between the reaction tube and the vacuum line.[1] Thus an evacuated system containing scandium, iodine, and perhaps a very small quantity of air was achieved. Before starting the reaction, the iodine was transferred to the lower end of the reaction tube by sublimation. For the preparation of scandium triiodide, about one-half to one atmosphere of iodine over the hot reaction zone of the container was achieved by heating the lower end of the reaction tube to 120-180° while the upper end was maintained at about 980°. This temperature differential was provided by two independently controlled 12 in. long, cylindrical resistance furnaces mounted vertically and butted together with asbestos tape used as insulation in the junction zone. The reaction tube was held in place by packed Fiberfrax (Carborundum Co.).

In a typical preparation, about 35 grams of ScI_3 were prepared. Some of the product remained in the tungsten crucible, but most collected in the hot-cold junction region of the reaction tube. Since some oxide or oxyiodide might be present as well as excess iodine, the ScI_3 was usually sublimed twice to insure a pure product. It was found that

---

[1] All temperatures are in degrees Centigrade unless otherwise noted.

the material could be conveniently sublimed at 680° in high vacuum. At first it was sublimed in fused silica, but when it was found that the melting point of ScI_3 could be raised 10° by sublimation in tantalum, this was used exclusively. The sublimed product was bright yellow and appeared very crystalline. It melted at 952°, which was considerably higher than a value of 920° tabulated by Brown (24). Analyses of the ScI_3 samples gave iodine to metal ratios of 2.99 ± 0.02 and material balances of 100.0 ± 0.2 %.

The ScI_3 and other materials to be described were susceptible to attack by oxygen and moisture. Therefore, storage has been under either vacuum or an inert atmosphere of argon. All transfers and handling procedures were carried out in an argon-filled glove box in which the argon was continually circulated through a Linde Molecular Sieve to insure its dryness. The absence of moisture was further assured by the maintenance of an open pan of P_2O_5 in the glove box. An evacuable port was used for entry, thereby reducing the possibility of contamination and the time required for entry.

Preparation of $ScBr_3$

Initially an attempt was made to prepare scandium tribromide from Sc_2O_3 and NH_4Br in an Ar stream by the reaction

$$Sc_2O_3(s) + 6\ NH_4Br(s) \ = \ 2\ ScBr_3(s) + 3\ H_2O(g) + 6\ NH_3(g)$$

which has been found useful in the preparation of several rare earth tribromides at about 250°. Here, the enthalpy of formation of Sc_2O_3 is higher than those rare earth cases. The gaseous products on the right side of the reaction indicated that entropy considerations might help the reaction to become thermodynamically favorable at higher temperatures. Unfortunately, the reaction failed to proceed satisfactorily below 400° in this case. The NH_4Br was too volatile at this temperature and was moved rather rapidly out of the reaction zone by the argon flow. Thus, $ScBr_3$ was prepared from the elements at 1000° in a fused silica apparatus which was similar to that described previously for the preparation of ScI_3. A fused silica rather than tungsten crucible was used. An adequate bromine pressure was obtained from liquid Br_2 in a finger at room temperature at the lower end of the apparatus. At the end of the reaction, the bromine was frozen and the ampule was sealed to remove excess bromine. Several sublimations of the product in tantalum at 700° gave a beautiful white crystalline product which melted at 969°. For comparison, Brewer (25) estimated 960° and Spedding and Daane (26) listed 948°. The $ScBr_3$, upon analysis, gave bromine to metal ratios of 3.00 ± 0.02 and material balances of $100.0 \pm 0.2\%$.

Analytical Methods

Determination of scandium, iodide, bromide, and chloride

Samples for analyses were usually placed in small glass vials and capped in the argon-filled glove box. These sample containers then were weighed in air, and the sample weights were determined by subtraction of the weights of the empty sample containers in air. The additional weight of argon was corrected for by subtracting the difference in weights of a duplicate sample vial containing argon and then air from the sample weight.

The determination of scandium was by titration with EDTA using xylenol orange as the indicator in an acetic acid-sodium acetate buffer at pH 4.0 (27). Iodide and bromide were determined volumetrically using standard silver nitrate solution and Eosin Y as indicator. In those few instances where chloride was determined, this was done gravimetrically by precipitation with silver nitrate, drying, and weighing as AgCl.

Some difficulties were encountered in the dissolution of the various reduced samples for subsequent analyses because of the extremely vigorous reaction with water or dilute (about 1-3 % by volume) acetic acid solutions. Spattering during the solution and the probable loss of small amounts of gaseous hydrogen halides initially gave unacceptably low total sample weights. These problems were largely overcome in two ways. Most commonly, the samples were handled as indicated above and the initial dissolution was accomplished in a few milliliters of absolute ethanol followed by slow addition of one to three percent by volume acetic acid. Alternatively, a sample was loaded in the glove box into an evacuable Pyrex sample container. The section in which the sample was placed was a length of 5 mm. o.d. Pyrex tube, and, upon evacuation, this section was sealed off using a hand torch. This was weighed in air, then opened in the glove box, the sample emptied into an evacuable container, and the pieces of the small sample container carefully added so as not to lose small pieces of glass, since the container weight was needed to obtain the sample weight. This larger sample container consisted of a lower section 1.5 in. o.d. x 6 in. and was connected to the upper section by standard ground glass joints. The upper section was fitted with a stopcock and a ball joint for connection to a vacuum line. This container was subsequently evacuated, and finally the sample was dissolved by addition of dilute acetic acid from a funnel into the closed container via a stopcock. Presumably, the closed container prevented loss of sample by spattering and any hydrogen halide evolved redissolved by washing the container well before it was opened and its contents transferred. Either method seemed suitable, but the use of absolute ethanol was much faster. The analytical results were considered reliable if the material balance totaled

$100.0 \pm 0.3\%$.

It should be pointed out that for the fully reduced scandium bromide or chloride samples material balances as low as 98.5% were common. The possibility of contamination by oxide was considered, and in a few cases where a leak had occurred there were indications of this. In these samples, a slight pink coloration of the normally black samples was noticed. In fact, in one particularly bad sample, very thin crystals of the material were obtained. These were shown to be ScOBr by allowing stoichiometric quantities of scandium oxide and $ScBr_3$ to react in tantalum at 1000°. The product gave a powder pattern that was the same as that obtained for the pink crystals. Normally the samples gave no visual hint of contamination, but powder patterns of the most reduced samples sometimes had traces of the strongest lines of ScOBr. The poor weight checks could be attributed in part to the fact that there was always a few milligrams of insoluble residue in solutions of fully reduced material. A few milligrams of unanalyzed material subtracted from the original sample weight would have given rather good weight checks. For example, 12 milligrams of insoluble material for a 0.8 gram sample should lead to a 98.5% material recovery. The exact make-up of the insoluble residue is uncertain, but three possible contributors are ScOBr, Ta, or finely divided scandium. ScOBr is sparingly soluble in dilute acetic acid, tantalum (possibly from the scandium metal used or the container) is insoluble, and scandium metal can be somewhat resistant to solution. When scandium metal is dissolved in dilute HCl, finely divided black particles result which only slowly dissolve. Scandium metal in dilute HNO_3 forms a black coating and becomes passive to further attack. From the above observations, it seems reasonable that most of the difference in the material balance resulted from insoluble (and unanalyzed) residue and that the material balances were much better than the 98.5% determined for samples of $ScBr_{1.5}$ and $ScCl_{1.5}$.

X-ray powder pattern determinations

Powdered samples were loaded into 0.3 mm. Lindeman glass capillaries which were sealed with Apiezon Q in the glove box, and later sealed with a gas-oxygen hand torch. Diffraction patterns were determined using a Phillips Debye-Scherrer camera with a diameter of 114.59 mm. The samples were exposed Cu Kα radiation which had passed through a Ni filter.

Determination of the Phase Diagrams

Methods employed for the determination of the temperature versus composition phase diagrams were thermal analysis and equilibration which were supported analytically by chemical analysis and X-ray powder diffraction patterns. Since the techniques used have been described in detail by the author elsewhere (28), an abbreviated version is presented here.

Thermal analyses

In a typical thermal analysis as performed in this work, a sample in tantalum with a thermocouple in good thermal contact was cooled at a regular rate such that the junction potential of the thermocouple was recorded on a strip chart recorder. Since standard tables were available for the direct conversion of the junction potentials of the thermocouples to temperature, a plot of temperature versus time was generated. Thermal processes in the sample were recorded as a change in slope in the temperature versus time curve. Six pieces of equipment were required for the thermal analysis experiments: a sample container providing a thermocouple seat, an evacuable apparatus designed to protect the sample container from attack by air at elevated temperatures and to prevent a thermal gradient over the sample, a furnace, a temperature controller, a strip chart recorder, and a potentiometer.

The tantalum sample containers were designed such that they could be sealed prior to use since the scandium trihalides were somewhat volatile at temperatures near their melting points. Entry was provided by a 5/32 in. i.d. tantalum tube initially three inches long which could be sealed after a sample was loaded. A 5/32 in. i.d. tantalum tube (closed at the sample end) extended into the sample and provided a seat for the chromel-alumel thermocouple.

Druding and Corbett (12) have essentially described the evacuable apparatus indicated above. This piece of equipment consisted of two sections connected by standard taper joints. The fused silica lower section was provided with a well-evacuated jacket to help slow the cooling rate of the sample from high temperatures which was in turn sheathed in platinum sheet so as to provide a radiation shield and to further insure an even temperature distribution in the sample zone. The Pyrex upper section provided entrance for the thermocouple and connecting facilities to a vacuum line. When in use, the jacketed portion of the fused silica section was positioned in a Marshall tube furnace which was lined with a piece of Inconel pipe three inches in diameter to provide even heating. This was grounded in order to reduce electronic interference in the temperature recording process. Temperature control was provided by a Minneapolis-Honeywell Brown Electronik Indicating Proportionating Controller. A Bristol Model 560 Dynamaster strip chart recorder was used to plot the sample thermocouple potential. A Rubicon potentiometer was used to obtain absolute potentials for conversion to temperature.

For a typical thermal analysis run, 3.0 to 4.5 grams of either $ScBr_3$ or ScI_3 were placed in a weighed tantalum crucible (previously cleaned by induction heating under dynamic vacuum) in the glove box along with the desired quantity of scandium metal. The entrance port was crimped shut and the crucible was placed in a stoppered sample tube for transport to the tantalum welder. Transfer of the crucible from the stoppered sample tube to the welder for evacuation and subsequent welding under argon or helium was accomplished as quickly as possible (less than 15 seconds). The closed crucible was then reweighed to obtain a close approximation of the weight of salt added, neglecting the small argon correction. This was then placed in the fused silica apparatus previously described, the thermocouple placement secured, and the apparatus evacuated prior to placement in the Marshall furnace since this was normally preheated.

The thermal analyses were made under dynamic (oil pump) vacuum since previous experience had indicated contamination to be less likely than by either static vacuum or under argon. The sample was equilibrated for varying periods of time before cooling, depending on the amount of metal to be dissolved. Normally about one hour seemed sufficient, but for the larger metal additions six to eight hours were sometimes used. At least two checks were made on thermal halts observed at each composition. These were found to be reproducible within one degree for a given run. Details on techniques such as controlling the cooling rate and the reduction of supercooling effects have been covered elsewhere by the author as indicated earlier. A given crucible was used for four or five compositions by simply cutting off the tip of the entry port in the dry box, adding a weighed quantity of scandium, and then rewelding the crucible. At the end of a run a portion of the sample was analyzed as indicated in the Analytical Methods section as a check. Discrepancies were usually less than 0.3 mole % of that calculated from the amounts of salt and metal added.

Equilibrations

The equilibrations for the limiting solubility of the scandium in ScX_3 (where X may represent Cl, Br, or I) were carried out in sealed 1/4 in. i.d. x 3 in. tantalum tubes at temperatures above the various incongruent melting points of the subhalides formed. These sample containers were sealed by a procedure that was similar to that described for sealing crucibles in the previous section except that in this case a section of tube several inches long was crimped shut in order to further minimize contamination during the transfer of the sample containers from the glove box to the welder and bent over so as to provide a hanger for later suspension in the equilibration apparatus.

The apparatus used for the equilibrations was that described by Mee (29) in which the sample was suspended from a hook by a tantalum wire such that the tip of a chromel-alumel thermocouple was in contact with the sample. Because scandium trihalides are highly volatile at temperatures near their melting points, the samples were melted and the containers crimped down to the level of the sample before the equilibration was begun. The equilibration was performed at constant temperature (± 1° as regulated by a Brown controller) under dynamic vacuum for periods ranging from 12 to 36 hours. An equilibration was terminated by rotating the supporting hook to allow the sample to drop into a room temperature reservoir of silicone oil containing glass wool to break the fall of the sample. The reduced material was separated from the incompletely consumed piece of scandium and analyzed as described in the Analytical Methods section.

After the phase diagrams had been outlined, subhalides were normally prepared by long term (3 to 10 days) equilibration at a temperature 15° to 75° below the peritectic temperature. These were carried out in a sealed tantalum tube in an evacuated fused silica ampule placed in a horizontal 12 in. cylindrical resistance furnace and the temperature was monitored with an additional thermocouple positioned next to the sample.

Resistivity Measurements

Resistivity measurements were made on a 0.25 in. diameter rod of composition $ScI_{2.23}$ using a four probe AC method. Both the technique used in growing the sample rod and the apparatus used in obtaining the resistivity measurements have been described by Corbett, Sallach, and Lokken (30) and will be treated only briefly here. Because $ScI_{2.15}$ melted incongruently, the preparation of a rod for resistivity measurements presented difficulties somewhat circumvented by Sallach. Using his technique and apparatus with a few slight modifications, several suitable rods were obtained after a protracted effort. The method involved very slowly lowering a fused silica apparatus (containing the sample in tantalum) through a thermal gradient of a few degrees per centimeter such that the thermal gradient spanned the peritectic temperature (892°) of $ScI_{2.15}$. The gradient was provided by dividing a 15 in. Marshall furnace into two sections by a transite baffle with a hole just large enough for insertion of the lower end of the fused silica apparatus. The lower section of the furnace was shunted using a 25 ohm power resistor across the furnace windings in that section. A 2.00 in. o.d. Inconel pipe was used in the upper section to reduce uneven heating. Similarly a 0.625 in. i.d. stainless steel pipe was used in the lower section. In this way, the furnace temperatures could be adjusted such that three inches above the baffle the temperature was 8°-10° above 892° and three inches below the baffle the temperature was about 8°-10° below 892°. Most of the gradient was in a narrow region just below the baffle.

The tantalum sample container was designed so as to allow a physical separation of a reservoir of excess scandium from that portion of the melt from which the rod was grown. During the descent of the sample through the thermal gradient, the local temperature was monitored by thermocouples affixed to both ends of the section in which the rod was contained. Experimentally, the sample was initially equilibrated for 24 hours at a temperature well above the peritectic temperature, then lowered through the temperature gradient at a rate of 0.2 in. every two hours. Conceptually, as $ScI_{2.15}$ crystallized, the melt locally became richer in ScI_3, then dissolved more scandium until equilibrium was again approached. Repetition of the process produced a homogeneous rod about three inches in length which could be satisfactorily used for measurements.

Since the sample was very sensitive to air, it was placed in a sample holder in an apparatus also designed by Sallach and rewired before the measurements were made. The sample rod was held in a Lavite block by stainless steel supports at each end which also served as electrical terminals in the primary circuit. Small discs of scandium metal were inserted at each end to reduce the possibility of reaction of the sample with the stainless steel or rectification. Also, thin rolls of tantalum were inserted between the sample and the stainless steel holder where these overlapped. Tungsten probes 1/2 in. apart were inserted into the side of the sample, and the voltage drop between these was measured.

Experimentally, a current of some fixed level (300, 500, or 750 ma.) at a fixed frequency (100, 300, or 500 cps.) was passed in a circuit including the sample, a standard resistor (0.05989 ohm), a 15 ohm load resistor, and a milliammeter. The signal was imposed by a Hewlett-Packard Model 200 CD oscillator and amplified by a Heathkit Model AA-81 power amplifier. Signals from the potential leads across the sample and the standard resistor were passed through a switch so as to be alternately amplified by a Type 122 Tektronix Low Level Preamplifier, and the voltage was measured using a Hewlett-Packard Model 400 H vacuum tube voltmeter. An oscilloscope was used to monitor the wave form of the signal during the voltage measurements. This was critical in that under some conditions poor wave forms were observed and thus inaccurate voltage measurements would have resulted had these circumstances not been corrected.

Since the internal resistance of the differential amplifier was in the order of a megohm and the resistances across the sample and standard resistor were less than 0.25 ohm, negligible current was drawn by the pick-up circuit across either. Hence, the current level in the primary circuit remained constant during the measurement. The resistance of the standard resistor was known, the voltage across its terminals was measured, and an accurate value for the current level in the primary circuit was calculated using

Ohm's law. Then, with the calculated current level and a measured voltage across the sample, the resistance of the sample was calculated. The resistivity of the sample was calculated from the relation

$$\rho = \frac{\pi r^2}{L} R(\text{sample})$$

where ρ is the resistivity, r is the radius of the rod in centimeters, L is the length of rod between the voltage probes, and R is the resistance of the sample. Measurements were made at several temperatures by placing the sample apparatus in a large dewar using hot water, liquid nitrogen, and various slush baths (CCl_4, diethyl malonate, Dry Ice-acetone, and n-pentane). The sample temperature was monitored by chromel-alumel thermocouples positioned at each end of the sample rod. Some of the problems in making these resistivity measurements will be discussed later.

Magnetic Susceptibility Measurements

Magnetic susceptibility data were obtained using the Faraday balance described by Converse (31) over the temperature ranges 77°-345° K for $ScI_{2.15}$ and 77°-300° K for $ScBr_{1.5}$. Measurements were made at five field strengths and susceptibilities at infinite field were obtained using a Honda-Owen plot.

Samples were loaded into a small Teflon bucket with a screw-in cap in the glove box. Diamagnetic corrections applied included a correction for the bucket.

EXPERIMENTAL RESULTS AND DISCUSSION

Organization of this section has been difficult because of the diversity of both the experiments performed and the basic differences in the iodide and bromide systems investigated. The course followed has been to separate the ScI_3-Sc system and the discussion of related iodides from those of the $ScBr_3$-Sc system and related systems except where their comparison seems useful. For this reason, the presentation of the cryoscopic data for the ScI_3-Sc system has been deferred until the $ScBr_3$-Sc phase diagram has been discussed, thus allowing the simultaneous treatment of data from both systems.

The ScI_3-Sc System and Related Iodides

The ScI_3-Sc phase diagram

The temperature versus composition diagram for the ScI_3-Sc system is shown in Figure 1. Cooling curve (thermal analysis) results are indicated by circles, and equilibration results are indicated by □'s; the data from both may be found in the Appendix. Pure ScI_3 melted at 952° and the addition of Sc metal depressed this melting point monotonically until the eutectic temperature of 847° (composition of 15.0 mole % scandium) was reached. Good thermal analysis data in the vicinity of the eutectic composition were difficult to obtain as indicated by the depressed liquidus arrests in this region.

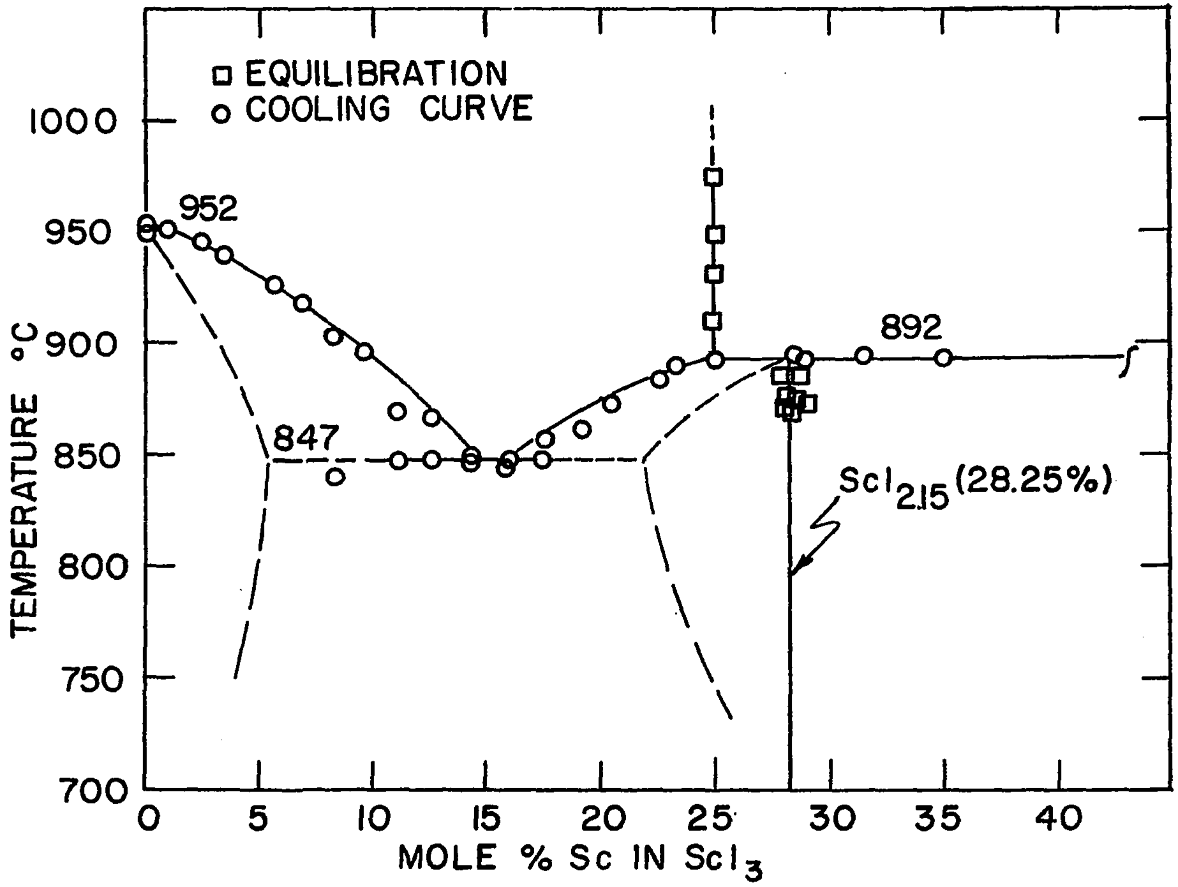


Figure 1. The phase diagram of the scandium(III) iodide-scandium system

These likely were supercooled, though the record of the thermal arrests for compositions near the eutectic showed no obvious indication of this, because the liquidus was supercooled at compositions less rich in Sc. Since the thermal phenomenon associated with the liquidus in the eutectic region is fairly weak, this should not be regarded as unusual. As a result, the liquidus probably should be drawn so as to intersect the eutectic about 1 mole % beyond the point of intersection shown. The thermal arrest corresponding to the eutectic tended to fade rather rapidly as the composition varied on either side of the eutectic composition. Only a very weak thermal arrest was observed at 8.28 mole % Sc and 839°; at 20.50 mole % Sc no eutectic halt was observed. The disappearance of the eutectic halts on both sides of the eutectic serves as evidence for regions of solid solution which have been rather arbitrarily indicated by the dashed lines. Further evidence at compositions near $ScI_{2.15}$ will be presented in the section on the stoichiometry of the subiodide.

Beyond the eutectic composition, the liquidus was found to rise until the solubility limit at the peritectic point of 25.0 mole % Sc and 892° was reached. Equilibration data above 892° determined the solubility limit of Sc in ScI_3 as indicated by the nearly vertical line at 25.0 mole % Sc. The liquidus properly intersected the solubility limit, thus giving an independent check on the peritectic composition. Thermal analyses of compositions beyond 25.0 mole % gave thermal arrests only at 892° since the equilibrium melt composition above this temperature was unchanged by additional metal. Equilibration data obtained at temperatures below 892° showed that the limiting composition was 28.25 ± 0.5 mole % Sc ($ScI_{2.15 \pm 0.02}$) with the range of possible errors estimated from observed scatter of data.

The scandium subiodide is a dark, nearly achromatic material with a suggestion of purple in appearance. From the phase diagram, $ScI_{2.15}$ was found to melt incongruently at 892° to give a liquid of composition $ScI_{2.25}$ and solid scandium metal.

Normally, the existence of a new compound or phase may easily be shown by the appearance of lines in the X-ray diffraction photographs of powdered sample which cannot be assigned to the starting materials, in this case ScI_3 and Sc. No Sc metal lines were observed in the samples. However, although the diffraction pattern for $ScI_{2.15}$ seemed to exhibit some new lines, many of the line positions were unchanged from those in ScI_3. In addition, the X-ray diffraction pattern of $ScI_{2.15}$ was similar to those of TiI_2 and VI_2 which have the CdI_2-type structure. All lines of $ScI_{2.15}$ could be accounted for by assuming a hexagonal structure with $a_o = 4.08$ Å. and $c_o = 6.97$ Å. ScI_3 has the closely related hexagonal BiI_3-type structure with a_o = 4.125 Å. and c_o = 6.805 Å. These structures consist of hexagonal close-packed iodide layers with the cations occupying the octahedral vacancies in alternate layers. In BiI_3, cations fill two-thirds of these octahedral holes; in CdI_2 all the octahedral holes are filled.

A comparison of the lattice parameters for ScI_3 and $ScI_{2.15}$ showed that in the latter a_o is decreased while c_o is increased. Thus, the position of some of the stronger lines in the X-ray powder diffraction patterns (see the Appendix) are fortuitously very nearly identical for the two structures.

The stoichiometry of the subiodide

Establishment of the CdI_2-type structure for $ScI_{2.15}$ suggested the obvious limiting composition should be $ScI_{2.00}$. Further, preliminary conductivity measurements indicated that $ScI_{2.15}$ was a good electrical conductor, and all the previously known metallic iodides (diiodides of La, Ce, Pr, Gd, and Th) were thought to be stoichiometric, at least as a limiting composition. Therefore, it seemed reasonable to try to make $ScI_{2.00}$. Toward this end, equilibrations were run for up to three weeks in the temperature range between the peritectic and eutectic, but no change in the apparent reduction limit was observed. Some samples were cooled slowly and allowed to remain at temperatures below 800° overnight without achieving any further reduction.

Since it was thought that equilibrations at lower temperatures might be hampered by rather poor diffusion, preparation of a small amount of ScI_2 was attempted by vapor deposition of small quantities of ScI_3 on chunks of Sc metal at 680° to 750°. Only a thin film of product could be obtained which was difficult to remove from the irregular metal chunks. This had the same pattern as $ScI_{2.15}$ with no apparent shift of line positions.

Next, it was thought that the observed composition might be related to energetically favorable ordering of the cations. An annealed sample cooled from 870° to 700° at a rate no greater than 4° per hour, and then somewhat more rapidly gave no indications of superstructure lines in the X-ray diffraction pattern even upon long exposure (over 24 hours). From this, it seems likely that about 5% of the cation positions are vacant and statistically disordered at the limiting composition and that the energy gained from increased entropy probably contributes toward stabilizing the subiodide.

A routine examination of the powder diffraction pattern of a thermal analysis sample of the approximate composition $ScI_{2.25}$ unexpectedly showed some changes in the relative intensities of some lines from those in $ScI_{2.15}$. This sample had been essentially quenched by removal from a hot furnace, and its exact composition was not known, but it prompted questions about possible ordering at compositions intermediate between ScI_3 and $ScI_{2.15}$ though no additional phases were indicated in the phase diagram. The possibility that a smooth transition from ScI_3 (two-thirds of the octahedral vacancies filled by cations) to $ScI_{2.15}$ (about 95% cationic occupancy) with a correspondingly gradual change in lattice parameters also was considered. Accordingly, samples of intermediate compositions $ScI_{2.75}$, $ScI_{2.60}$, $ScI_{2.46}$, and $ScI_{2.30}$ were made up in sealed tantalum containers, melted, and allowed to remain molten so as to dissolve the scandium metal, and then quenched to room temperature so as to minimize phase separation. These containers were then crimped down to the sample levels so as to reduce excess volume from the containers. The samples were gradually heated to 790°, annealed at this temperature for several days, and subsequently gradually cooled over several days. The resulting samples were visually homogeneous, and their coloration increased with scandium content. Powder diffraction patterns of the samples are reproduced in Figure 2. The data are found in Table 1, which may prove more helpful in the following discussion. Indexing of the patterns for the limiting compositions is also shown in the table, but indices for all the possible lines in a hexagonal system with these cell parameters are not shown. Several points need to be recalled to facilitate discussion of the data in Table 1. First, the lattice parameters for ScI_3 are $a_o = 4.08$ A., $c_o = 6.97$ A., and for

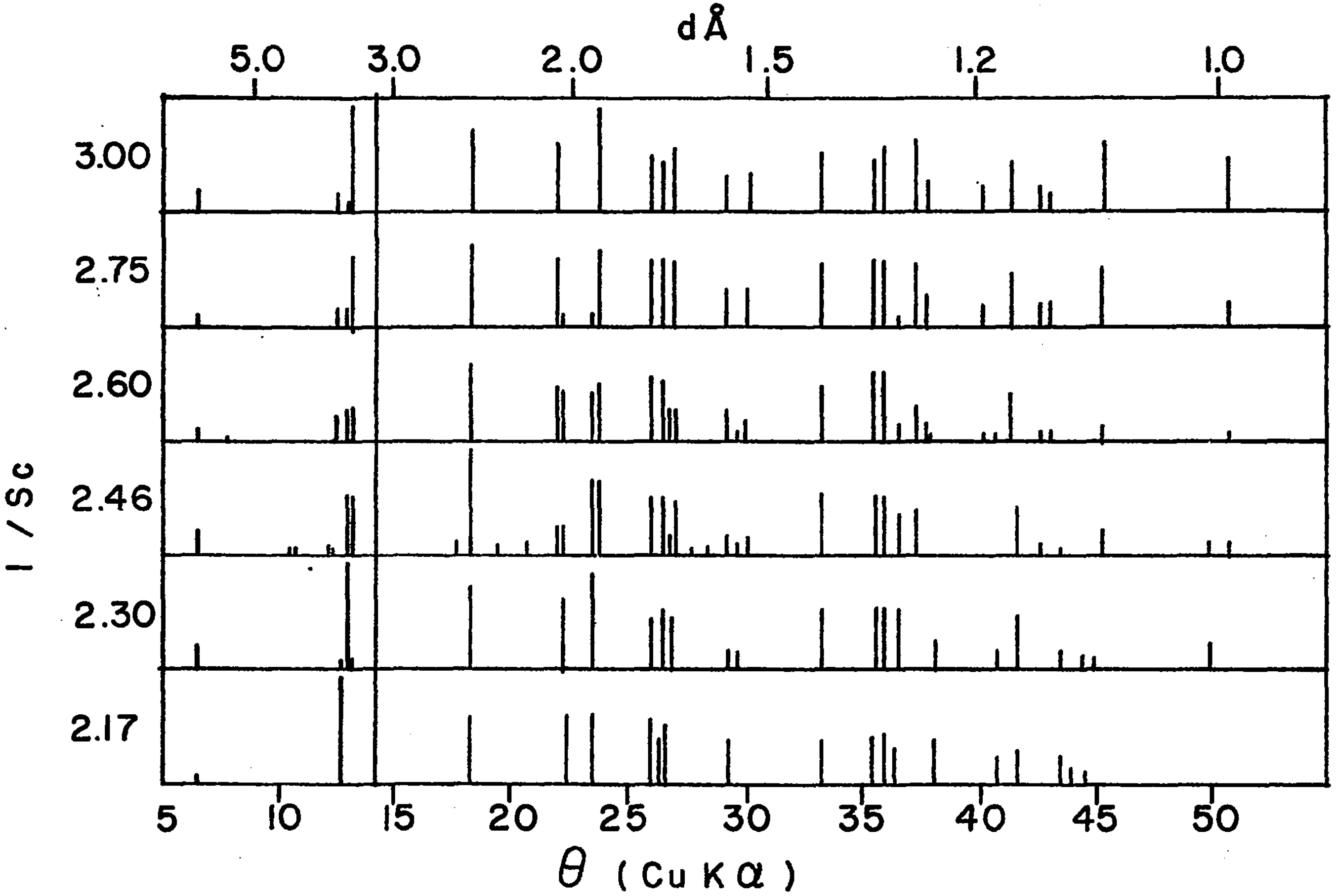


Figure 2. The X-ray diffraction data for $ScI_{3.00}$, $ScI_{2.75}$, $ScI_{2.60}$, $ScI_{2.46}$, $ScI_{2.30}$, and $ScI_{2.17}$

Table 1. A Comparison of X-ray Powder Diffraction Data for Several Scandium Iodide Compositions

hkℓ for ScI_3	ScI_3 d(Å)	ScI_3 I/I_o	$ScI_{2.75}$ d(Å)	$ScI_{2.75}$ I/I_o	$ScI_{2.60}$ d(Å)	$ScI_{2.60}$ I/I_o	$ScI_{2.46}$ d(Å)	$ScI_{2.46}$ I/I_o	$ScI_{2.30}$ d(Å)	$ScI_{2.30}$ I/I_o	$ScI_{2.15}$ d(Å)	$ScI_{2.15}$ I/I_o	hkℓ for $ScI_{2.15}$
001	6.8	20	6.8	10	6.8	10	6.8	20	6.9	20	6.9	15	001
	--	--	--	--	4.2	?	4.2	8	--	--	--	--	
	--	--	--	--	--	--	3.63	7	--	--	--	--	
100	3.57	15	3.57	15	3.57	20	--	--	3.51	5	3.51	50 90	100
	--	--	3.45	15	3.46	25	3.45	50	3.48	90	3.485	50	002
002	3.39	90	3.39	60	3.39	25	3.39	50	3.39	5	--	--	
101	3.15	100	3.15	100	3.15	100	3.15	100	3.15	100	3.15	100	101
	--	--	--	--	--	--	2.55	10	--	--	--	--	
102	2.455	70	2.452	70	2.46	65	2.46	90	2.46	70	2.48	65	102
	--	--	--	--	--	--	2.32	5	--	--	--	--	
	--	--	--	--	--	--	2.18	10	--	--	--	--	
110	2.055	60	2.058	60	2.055	45	2.055	25	--	--	--	--	
	--	--	2.04	10	2.04	40	2.04	25	2.04	60	2.04	60	110
	--	--	--	--	--	--	1.995	5	--	--	--	--	
	--	--	1.935	10	1.94	40	1.937	65	1.93	80	1.94	60	103
103	1.91	90	1.91	65	1.91	45	1.910	65	--	--	--	--	
112	1.76	50	1.761	55	1.76	55	1.76	50	1.76	45	1.76	40	112
201	1.725	45	1.73	55	1.73	50	1.73	50	1.73	50	1.741	50	004
	--	--	--	--	1.71	25	1.71	15	1.709	45	1.711	35	201
004	1.698	55	1.698	55	1.70	25	1.698	45	--	--	--	--	
	--	--	--	--	--	--	1.66	4	--	--	--	--	
	--	--	--	--	--	--	1.62	4	--	--	--	--	
202	1.58	30	1.58	30	1.58	25	1.58	15	1.576	15	1.579	35	202
	--	--	--	--	1.56	5	1.56	9	1.558	15	--	--	104
104	1.535	30	1.539	30	1.538	15	1.536	15	--	--	--	--	113
203	1.404	50	1.405	50	1.405	45	1.405	50	1.405	50	1.407	35	203
121	1.326	45	1.327	55	1.327	60	1.325	50	1.324	50	1.329	40	114
114	1.312	55	1.313	55	1.313	60	1.31	50	1.311	50	1.313	40	211
	--	--	1.292	5	1.292	15	1.292	35	1.293	50	1.300	30	105
105	1.271	60	1.272	50	1.273	25	1.272	35	--	--	--	--	
212	1.256	25	1.252	20	1.259	10	--	--	1.294	25	1.250	35	212

$ScI_{2.15}$, a_o = 4.125 A., c_o = 6.805 A. Second, for a hexagonal system a = b $\neq$ c and in calculating d-values, terms involving a and c are not mixed since

$$\frac{1}{d^2_{hkl}} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \frac{l^2}{c^2} .$$

Since a_o and c_o change in opposite directions for the two limiting compositions, for a given hkl assignment the best distinctions in d-values can be expected for those indices heavily weighted by either h and k or l. Thus, considerable differences in d-values are noted for such lines as 002, 100, 004, and 104 while almost no change is evident in such lines as 110, 112, and 202. A fortuitous similarity (best seen in Figure 2) is the conspicuous "triplet" made up of the 112, 201, and 004 lines in the patterns of the limiting compositions. This is accounted for by the reversal in positions of the 201 and 004 lines due to the changes in lattice constants.

The patterns for $ScI_{2.75}$, $ScI_{2.60}$, and $ScI_{2.46}$ seem to represent mixtures of the two limiting compositions because of the increasing intensities of such characteristic lines in $ScI_{2.15}$ as the 002, 110, 103, and 105 with added Sc content. Interestingly, some indication of ordering in one or both limiting phases may be seen in the $ScI_{2.60}$ and especially in the $ScI_{2.46}$ pattern by the appearance of several weak lines.

Some attempts were made to account for these lines by assuming superstructures for the limiting phases, but so many possible lines could be generated in this way that one could account for almost anything. A small distortion with a resulting decrease in symmetry could also be a source of the new lines.

In the pattern for $ScI_{2.30}$, only a very small amount of ScI_3 can be present as indicated by the trace presence of the 002 line at d = 3.39 A. There are several indications that the lattice parameters (the c_o parameter in particular) may have changed compared with that in $ScI_{2.15}$. First the d-values of the 004 and 105 lines seem to be decreased somewhat. Also, the 100 and 002 lines seem nearly to have coalesced--at least there is little indication of the splitting of these strong lines as in the $ScI_{2.15}$ pattern. Finally it should be noted that the 104 line, which is absent in the $ScI_{2.15}$ pattern, is present. This would tend to support at least some homogeneity range for the subiodide phase. The faint presence of the 002 line of ScI_3 warns that the composition $ScI_{2.30}$ may be just outside the upper composition limit of this range, and it now seems likely that the equilibration limit of $ScI_{2.15}$ below the incongruent melting point represents the lower phase limit.

Resistivity data for the scandium subiodide

Shortly after the preparation of $ScI_{2.15}$, it was found to be a rather good conductor. The resistance across a manually pressed 1/4 in. pellet was found to be on the order of 900 ohms, as measured by a vacuum tube volt-ohmmeter. Annealing the pellet at 800° reduced the resistance to about 600 ohms. It was realized that contact resistance was a problem when insertion of thin leaves of scandium metal between the sample and the resistance probes reduced the measured resistance to 4 to 8 ohms, depending on the pressure applied mannually with the probes. Using a 1/2 in. evacuable stainless steel die and a hydraulic press, a pellet was obtained under a pressure of 18,000 lbs. per square inch applied for five minutes. The resulting pellet was about 1/4 in. thick, and the resistance across this was about 4 ohms at room temperature. Attempts to establish the temperature dependence of the resistance by making measurements at lower temperatures gave inconclusive results.

It was decided to make resistivity measurements by AC methods using the apparatus reported by Corbett, Sallach, and Lokken (30) and described in the Experimental Procedures section. The resistance data obtained on a sample of composition $ScI_{2.23}$ are to be found in the Appendix. The resistance data seemed fairly reproducible at different frequency and current levels. In Figure 3 the resistivity data calculated from the resistance measurements at 300 cps and 500 ma. are plotted versus absolute temperature. The resistivity was found to decrease nearly linearly from a value of 1.54 x

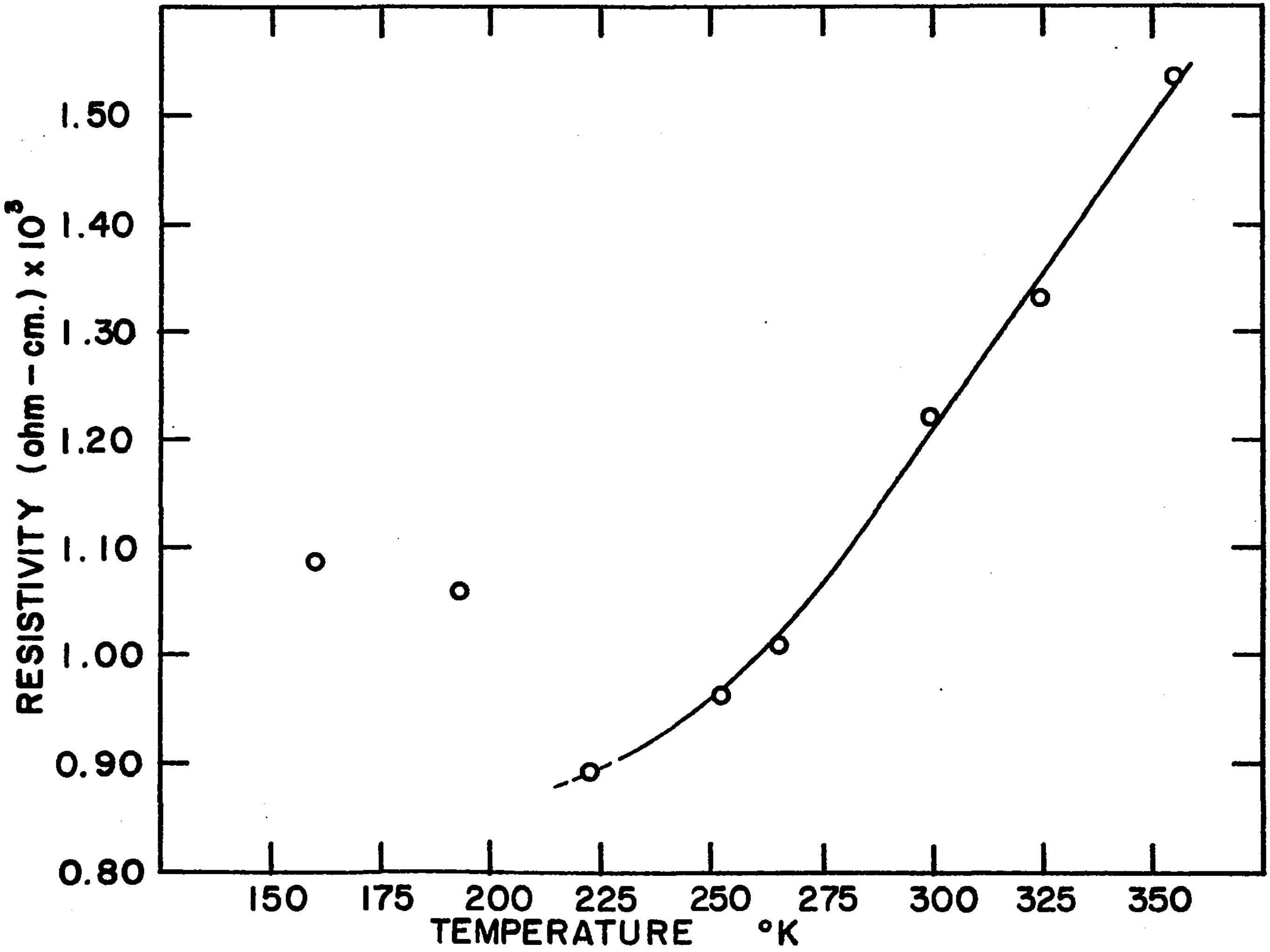


Figure 3. The temperature dependence of the resistivity of $ScI_{2.23}$

10^{-3} ohm-cm. at 355° K to 0.89 x 10^{-3} ohm-cm. at 222° K. The negative temperature dependence of the conductivity is characteristic of metallic conductors. The resistivity apparently increased at the two lowest temperatures employed. An attempt to obtain data using liquid nitrogen at 77° K was unsuccessful, perhaps because of poor probe-sample contacts or a crack in the sample rod. This sample was subsequently lost during attempted adjustments. As a consequence, the resistivity measurements were not rechecked and thus the results are not entirely satisfactory, although there is no reason to suppose that the results shown are not at least qualitatively correct.

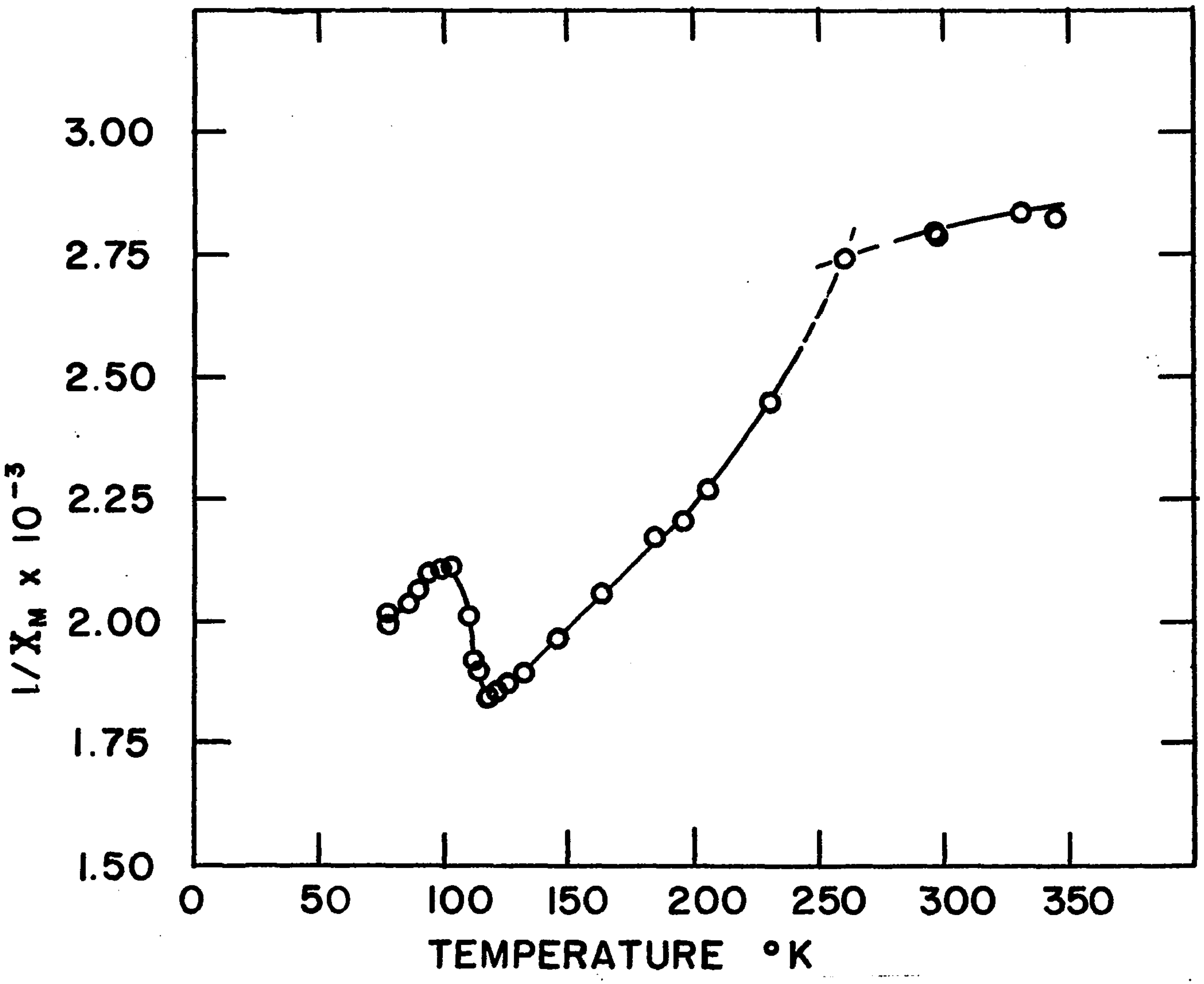
It is unfortunate that more data could not be obtained, but those presented were obtained only after very frustrating efforts. The scandium subiodide was found to be very susceptible to cleavage. Those rods in which the cleavage plane occurred perpendicular, or nearly so, to the rod length were always broken in the process of removal of the tantalum container. The cleavage plane in the rod used was oblique to the long axis of the rod. Mounting the rods in the sample holders accounted for the ruination of several specimens because the pressure applied to assure contact of the electrical probes to the sample sometimes cracked the specimen. The general fragility of the sample apparatus and the necessity for considerable handling further reduced the chances of a successful experiment. This partial list of the difficulties involved, together with doubts that very much additional information of intrinsic value could be obtained, led to the cancellation of further resistivity experiments.

Magnetic data for the scandium subiodide

The magnetic data for the scandium subiodide were expected to show a weak temperature-independent Pauli paramagnetism, analogous to such materials as LaI_2 and ThI_2 which exhibit room temperature χ_M values (corrected for the diamagnetism of the sample) of 115×10^{-6} and 50×10^{-6} emu. per mole, respectively (32, 33). Other materials that might be pertinent such as CeI_2, PrI_2, and GdI_2 have cationic cores with f-electrons which contribute largely to the observed susceptibilities and thus mask the expected Pauli contribution. The magnetic results for a sample of composition $ScI_{2.15}$, shown as a plot of $1/\chi_M$ versus T in Figure 4, were therefore somewhat unexpected. The data are tabulated in the Appendix. The molar susceptibility, χ_M, has been corrected with an estimated core diamagnetism of -122×10^{-6} emu. per mole (34). The value for χ_M of 359×10^{-6} emu. per mole obtained at room temperature is about three times the value reported for LaI_2, and assuming Curie law behavior, this would correspond to a magnetic moment of 0.92 β.

The data from 260° K to 345° K show only a small temperature dependence, but the temperature dependence at lower

Figure 4. The temperature dependence of the molar magnetic susceptibility of $ScI_{2.15}$



3.00
2.75
2.50
2.25
2.00
1.75
1.50
$1/\chi_M \times 10^{-3}$
0
50
100
150
200
250
300
350
TEMPERATURE °K

temperatures suggests the presence of some valence band (localized) electrons. An apparent transition occurs at about 250° K, below which the material becomes increasingly paramagnetic with decreasing temperature until the sharp transition at 118° K. This transition might ordinarily have been associated with antiferromagnetic ordering, but the reversal of this effect at 103° K would be difficult to explain, since experimental observation of such behavior has been rare. For example, CeAs has been found to show a similar magnetic anomaly (35), and it was suggested that this might be due to a weak antiferromagnetic ordering followed by a weak ferromagnetic effect, since an appropriate field dependence was observed. No such field dependence was observed in this case.

Supplementary evidence often quoted as supporting the presence of magnetic ordering has been the disappearance of the metal NMR signal at the Neel transition temperature. Members of Dr. Richard Barnes' group generously examined the ^{45}Sc NMR signal of a finely powdered sample of $ScI_{2.15}$ down to 77° K from well above the transition at 118° K. There was no disappearance of the signal below 118° K, but a slight broadening of the single peak may have occurred. This is not regarded as proof of the absence of magnetic ordering.

Resistances of TiI_2 and VI_2

Titanium diiodide was found difficult to prepare satisfactorily, and a discussion of its preparation and physical properties will be presented later. A suggestion for preparation of purer VI_2 may also be found in that same section. The resistances of samples of probably impure TiI_2 and VI_2 (CdI_2-types) were measured across manually pressed 1/4 in. pellets. For TiI_2, a resistance of about 700 ohms was measured, while VI_2 gave about 7,000 to 8,000 ohms. When it is recalled that $ScI_{2.15}$ gave a value of about 900 ohms by this method, it can be seen that the TiI_2 might well be metallic. The resistance of VI_2 indicates that it is probably a narrow gap semiconductor, but to check this, investigation of pure materials by more sophisticated techniques is obviously needed.

Discussion of the Properties of the Scandium Subiodide

Only a few iodides have been reported to be metallic conductors. These are LaI_2, CeI_2, PrI_2, GdI_2, and ThI_2 according to Corbett and co-workers (10, 11, 32). (There has been a report that TlI has undergone a transition to a metallic form at about 100 kilobars pressure (36), but since the reported energy gap between the valence and conduction bands at room temperature is about 3.5 ev., it is normally salt-like.) Resistivity measurements for the first two diiodides have been reported (30). $LaI_{2.00}$ was found to be a good metal with a low resistivity of 6 x 10^{-5} ohm-cm. at room temperature. Some difficulty was experienced in obtaining data for an incompletely reduced sample of the composition $CeI_{2.07}$ for which resistivities were obtained at only four temperatures. These ranged from 1.3 x 10^{-3} ohm-cm. at 153° K to 2.7 x 10^{-3} ohm-cm. at 300° K which paralleled fairly closely the results obtained for $ScI_{2.23}$. Since the two have different structures, it probably is not valid to compare their resistivities too closely. Because of difficulties similar to those reported here, Sallach was unable to obtain data for PrI_2.

For metallic materials. the band model is presently the most useful theoretical approach. Accordingly, some results from this model which are pertinent to the magnetic and resistivity data for metallic conductors are presented below. The band result

$$\chi_p \sim 3\ N\ \mu_B^2/2\ k\ T_F$$

shows the Pauli paramagnetic susceptibility to be related inversely to the Fermi temperature, which is $T_F = E_{F(0)}/k$. The Fermi energy in turn is related to the effective mass of the electron, m^*, by the relation

$$E_{F(0)} = (3\ \pi^2\ N)^{2/3}\ \hbar^2/2\ m^*.$$

The electrical conductivity, σ, is related to the effective mass of the electron by

$$\sigma = Ne^2 \tau/m^*$$

where τ is the relaxation time. Other terms in the above relations are N, the number of atoms, and μ_B, the Bohr magneton. A discussion of the above results may be found in Kittel (37). Of course, the expressions above hold best for the alkali metals, where a pure s-band is expected. They were introduced here so that, in principle, the properties of the subiodide could be discussed. The effective mass of the electron is considered to be related to the interaction of the band electrons with the crystal lattice. It is important here because it is directly proportional to the temperature-independent-paramagnetic susceptibility and indirectly proportional to the conductivity. High effective masses are commonly exhibited by narrow 3d-band conductors. Conceptually, energy bands become narrower as overlap of cationic orbitals decreases. Thus, the decrease in conductivity of CeI_2 compared to LaI_2 may reflect in part the expected contraction in the radial extentions of the 5d-orbitals going across the rare earth series in addition to the effect of CeI_3 in the incompletely reduced cerium sample. Also, other things being equal, the 5d-orbitals should extend further than 3d-orbitals, and $ScI_{2.15}$ might be expected to form a narrower band than LaI_2. A complicating factor in attempting to compare LaI_2

with $ScI_{2.15}$ is the fact that they are not isostructural.

The importance of the radial extension of the d-orbitals is further suggested by the resistances made on loosely pressed pellets of TiI_2 and VI_2 which imply that the conductivity of VI_2 is much less than that of TiI_2. The radial extension maxima of the 3d-orbitals for Sc, Ti, and V have been calculated to be 0.59 Å., 0.53 Å., and 0.48 Å., respectively (38). Direct comparison is made difficult by the increasing number of d-electrons for TiI_2 and VI_2. Additionally, nonstoichiometric materials (here defined as those which exhibit a composition range in a single phase region) also often exhibit high effective masses, presumably by interaction of the band electrons with lattice vacancies or altervalent ions in the lattice. Considering this, the presence of cation vacancies in $ScI_{2.15}$ would be expected to contribute toward a higher effective mass, a higher observed χ_M, and reduced conductivity.

A comparison of the magnetic data in Figure 4 with the resistivity data in Figure 3 is not enlightening. The magnetic anomaly at about 250° K is not reflected in the resistivity data. Similarly, the change in resistivity between 192° K and 222° K has no apparent counterpart in the magnetic data, although the benefit of hindsight and a little imagination may reveal a slight change in the slope of the magnetic data at about 195° K.

The observed room temperature magnetic moment would be unusually, but not impossibly high, if attributed entirely to a high effective electron mass for electrons in an unfilled band. However, the temperature dependence of the magnetic data below 250° K may indicate the presence of some valence band electrons. There is a possibility that the magnetic transition at about 250° K may reflect a change from band to valence electrons. If so, this should be reflected in the resistivity data, but none is now available for the same composition ($ScI_{2.15}$). This apparent conflict with the resistivity data for a sample of composition $ScI_{2.23}$ may be an indication that the subiodide properties change significantly with composition. Earlier it was pointed out that the X-ray powder diffraction data for a sample of composition $ScI_{2.30}$ indicated some change of the lattice parameters from those of $ScI_{2.15}$ and that one line unobserved in $ScI_{2.15}$ was present. Thus some discrepancies might be attributed to rather subtle structural distortions.

Preliminary Work on Titanium and Vanadium Diiodides

After most of the work of the ScI_3-Sc system was completed, interest in TiI_2 and VI_2 arose from the fact that both exhibit the CdI_2 structure found for the scandium subiodide. The consideration of decreasing radial extensions of the d-orbitals in the Sc-Ti-V series and unusual magnetic data for TiI_2 further increased interest in them. Work on these compounds must be considered preliminary, and the following introductory material and details on attempts to prepare pure TiI_2 are presented because published data are scarce and the information may prove useful to future workers in this area.

Very little had been done toward investigating the physical properties of these compounds, most probably because of the difficulty of their preparation in pure forms. Magnetic data at three temperatures had been obtained by Klemm and Grimm in 1942 (39). Their magnetic data for TiI_2(I), TiI_2(II), and VI_2 are listed below in Table 2.

Table 2. The magnetic data for titanium and vanadium diiodides

	χ_M (corrected for diamagnetism) x 10^6		
Compound	90° K	195° K	288° K
TiI_2(I)	250	350	380
TiI_2(II)	360	1800	1790
VI_2	9400	5700	4400

Assuming the Curie law to hold, the μ_{eff} values at room temperature for the three materials are 0.94, 2.03, and 3.20 β. The magnetic moment of VI_2 is considerably lower than the spin only value, but the temperature dependence of the data is at least in the right direction for a paramagnetic substance.

Recently, good crystals of red and black forms of VI_2 have been prepared by hot-to-cold-zone transport reactions by Schäfer et al. (40). Both forms have nearly the same magnetic data which corresponds very well to that given by Klemm except the new values are somewhat higher at 90° K. Curiously, Schäfer, et al. chose to report data only at the temperatures that Klemm did. They reported that the red form has the CdI_2-type structure and that the black form may have the $CdCl_2$-type structure, but this was unsupported with data. It would have been interesting to see whether the black form has the TiI_2(I) structure.

The range over which TiI_2(I) was nearly temperature independent suggested that it might be metallic, and it was toward checking this possibility that the work on the titanium iodides was directed. Later, it was discovered that Klemm and Basualdo (41) had reported additional magnetic data for material presumed to be TiI_2(II). In contrast to the data found in Table 2, this material seemed properly paramagnetic down to about 190° K, where a transition occurred. The value of χ_M dropped from about 2450×10^{-6} emu. at 190° K to about 1350×10^{-6} emu. at 120° K where a reversal was observed with χ_M rising to about 1460×10^{-6} emu. at 90° K. This reversal is somewhat uncertain because of a large hysteresis effect on warming the sample. On warming, the material did not become normally paramagnetic until 250° K, compared to 190° K observed on cooling. Because of this, there is the possibility that the reversal may be associated with the hysteresis, and it is doubtful that a useful analogy can be made with the magnetic anomaly observed for the scandium subiodide.

Preparation of TiI_2

The interrelation of the chemistry of the titanium iodides has been extensively investigated by Fast (42), and by other workers (43-45). The chief difficulty in the preparation of TiI_2 stems from the following processes which take place under vacuum in a sealed tube at sequentially higher temperatures, approximately as indicated.

$$3\ TiI_4(g) + Ti(s) \xrightarrow{330^\circ} 4\ TiI_3(s)$$

$$2\ TiI_3(s) \xrightarrow{440^\circ} TiI_2(s) + TiI_4(g)$$

$$TiI_4(g) + Ti(s) \xrightarrow{440^\circ} 2\ TiI_2(s)$$

$$2\ TiI_2(s) \xrightarrow{>480^\circ} TiI_4(g) + Ti(s)$$

Of course, reactions such as these do not just turn on or off at a specified temperature, and the results no doubt vary widely depending on conditions. Further, in the course of experiments at 550° serious attack of fused silica containers was observed. All the titanium iodides are sensitive to attack by oxygen or moisture, which has probably reduced interest in them.

Since preparation of TiI_2 by the disproportionation reaction 2 might be expected to yield contaminated product, attempts were made by direct reaction of Ti metal sheet at various temperatures with about 10 mm. pressure of TiI_4 by use of the technique applied in preparation of ScI_3 and $ScBr_3$. The product was a thin black layer on the Ti strips which at 560° was identified by X-ray powder data as the CdI_2-type of TiI_2 reported by Klemm and Grimm (46). Because the layer on the metal was very thin, only one gram quantities were prepared in this way. Below 500°, lines in the powder pattern of the product attributable to TiI_3 were observed. Thus titanium diiodide was prepared in the high temperature form (CdI_2 structure) by reaction of TiI_4 with excess titanium metal as turnings in a sealed tantalum reaction tube. Since the formation of TiI_2 was found to be slow, and because of the high vapor pressure over any remaining TiI_4, the reaction tube was equilibrated at 440° for several days before the temperature was gradually increased to 880° without giving X-ray powder evidence for titanium metal in the product. When excess space was allowed in a sample container above 900°, Ti metal lines were observed in the powder pattern. Still, the resulting material may not have been stoichiometric TiI_2. In samples of composition $TiI_{2.6}$ and $TiI_{2.0}$ (based on the original quantities of Ti + TiI_4), the last traces of metal were eliminated only by successive equilibrations at 600°, 800°, and 925°. These samples were closely confined and no Ti metal lines were observed even in the powder pattern of the 925° equilibration. The $TiI_{2.6}$ sample showed no lines other than those of pure TiI_2 and no shift in d-spacings for the X-ray powder lines could be discerned using the Debye-Scherrer technique. This may be evidence that extensive solid solution of TiI_3 in TiI_2 can occur.

In retrospect, had a copy of a presentation by Klemm, Holze, and Basualdo (41) been available earlier most of the above work would have been avoided. Klemm and Grimm (39, 46) had neglected to detail how pure forms of the two diiodides were obtained. In the later paper, it was indicated that the CdI_2-type form was obtained by the sublimation of crude TiI_2 in the presence of excess metal. The other form was obtained by the disproportionation of TiI_3 in excess metal at 550° after which TiI_2 was effectively sublimed in that it was collected in a cooler zone at 440°. This form, in retrospect, was observed by the author in an impure form by reaction of TiI_3 (and possibly a bit of TiI_4) with excess titanium metal in tantalum at 550°. The tube used was large enough to allow some material in the vapor phase and the product may have partially resulted from a disproportionation of TiI_3.

In conclusion, nearly pure TiI_2 of the CdI_2-type may be prepared by long equilibration of TiI_4 with excess Ti metal above 800° in a tantalum container of closely limited volume. The TiI_4 must be completely reduced by sufficiently long equilibration at about 400° (to avoid excessive pressure) before the reaction temperature is raised to 800°. The product might be used as suggested above to prepare pure CdI_2-type TiI_2. For preparation of the other form of TiI_2, the disproportionation of TiI_3 might be tried. The temperature of the condensation of the vapor species is probably critical, and this might be adjusted by experience. For convenience, a preparation of TiI_4 is given below, and both McCarley and Schäfer are referenced for preparation of pure VI_2.

Preparation of TiI_4

Thirty-five grams of titanium tetraiodide was prepared by the reaction of sufficient iodine with excess titanium (as turnings) in a sealed, evacuated ampule for several days at 170°. Before use, the resulting material was separated by sublimation from any TiI_3, oxide, or oxyiodide which may have formed.

Preparation of VI_2

Some material of the composition $VI_{2.3}$ was supplied by members of R. E. McCarley's research group which had been prepared as described by Berry, Smardzewskii, and McCarley

(47). Vanadium diiodide was prepared by removal of excess iodine from this material by heating at 350° under dynamic vacuum for 16 hours. In retrospect, better VI_2 could have been made by transport reaction as reported by Schäfer et al. (40).

The $ScBr_3$-Sc System

The $ScBr_3$-Sc phase diagram

The $ScBr_3$-Sc phase diagram is shown in Figure 5. The Appendix contains the thermal analysis and equilibration data that are used in the phase diagram. The diagram is similar to that reported for the ScI_3-Sc system. Before the eutectic the differences are small; $ScBr_3$ melted somewhat higher than ScI_3, at 969°, and there is an unexplained change in the slope of the liquidus at 851° and a composition of 15 mole % Sc in $ScBr_3$. This was discovered by the accumulation of thermal analysis data defining the liquidus, and the extremely weak thermal effect shown at 851° at several compositions was found only upon re-examination of thermal analysis curves. This halt seemed not to be present in pure $ScBr_3$, and it seemed weaker at 6.7 mole % Sc than at 10.2 or 12.8 % Sc. A premelted sample of composition 13.5 mole % Sc which was equilibrated overnight at 835°, and then quenched, showed no lines in the X-ray powder diffraction pattern other than $ScBr_3$ and a few very weak lines attributable to $ScBr_{1.5}$.

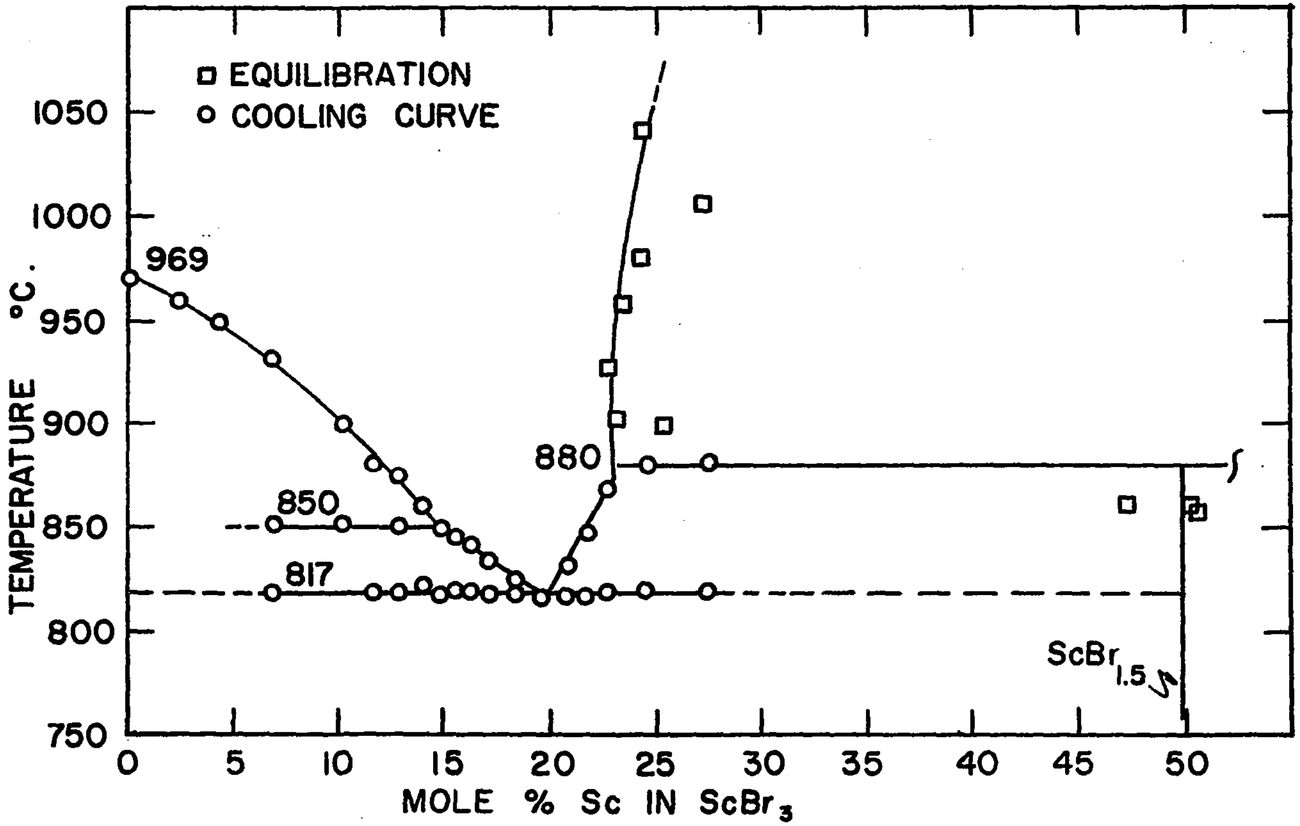


Figure 5. The phase diagram of the scandium(III) bromide-scandium system

Beyond the eutectic at 817° and 18.5 mole % Sc, the liquidus rises to a peritectic at 880° and 23.0 mole % Sc ($ScBr_{2.31}$) which is corroborated fairly well by the solubility limit determined by equilibrations of $ScBr_3$ with excess Sc. The most interesting feature of the phase diagram is the evidence for the unexpected formation of $ScBr_{1.5}$. The liquid composition in equilibrium with $ScBr_{1.5}$ at 860° is about $ScBr_{2.34}$, which means that some difficulty might be expected in keeping the liquid in good contact with the pieces of excess scandium metal so as to reduce all the liquid. Also, $ScBr_{1.5}$ turns out to be quite fibrous, reminiscent of, say, glass wool which may provide considerable surface area for the adsorption of small amounts of the liquid phase. It was found necessary to pull the initial product into fine pieces and to further equilibrate these pieces with small chunks of scandium metal to assure good contact with excess metal. Equilibration periods of up to one week were used. This procedure seemed virtually to eliminate $ScBr_3$ from the X-ray diffraction pattern of the result, but even with care in handling, the repeated equilibrations sometimes resulted in trace impurities of ScOBr which imparted a trace of purple to the product in contrast with the purest samples which appeared black. The composition of the subbromide has been established as $ScBr_{1.5 \pm 0.05}$. The uncertainty was caused by problems with insoluble impurities which have been discussed in the Experimental Procedures section.

Evaluation of cryoscopic data

For the dissolution of metals in their molten salts, under favorable circumstances, some information about the nature of the solute species may be obtained by consideration of cryoscopic data. Here, the following variation of the Clausius-Clapeyron equation was pertinent, assuming deviation from Henry's law is small for dilute solution.

$$\Delta H^{o}_{(fusion)} = -2.3\ R\ d\ \log X_{(solvent)}/dT = -4.576\ (slope)$$

For a nearly ideal solution, a good experimental enthalpy of fusion might be obtained cryoscopically if sufficient care and attention to purpose were made to obtain good data. Here it was felt that there were reasons to doubt this. The cryoscopic data used were those from the ScI_3-Sc and $ScBr_3$-Sc phase diagrams previously discussed. The data ran from about 0 to 14 mole % Sc in the trihalides but only a few were for less than 5 mole % metal; thus, extrapolation to infinite dilution was hardly possible. Also, the exact nature of the solute species was somewhat uncertain and solid solution probably causes further deviation from ideality. Thus the heats of fusion for the trihalides estimated by Brewer (25) to be 18 kcal./mole for ScI_3 and 19 kcal./mole for $ScBr_3$ have been used to calculate a slope represented by the straight lines drawn in Figures 6 and 7 for the iodide and bromide

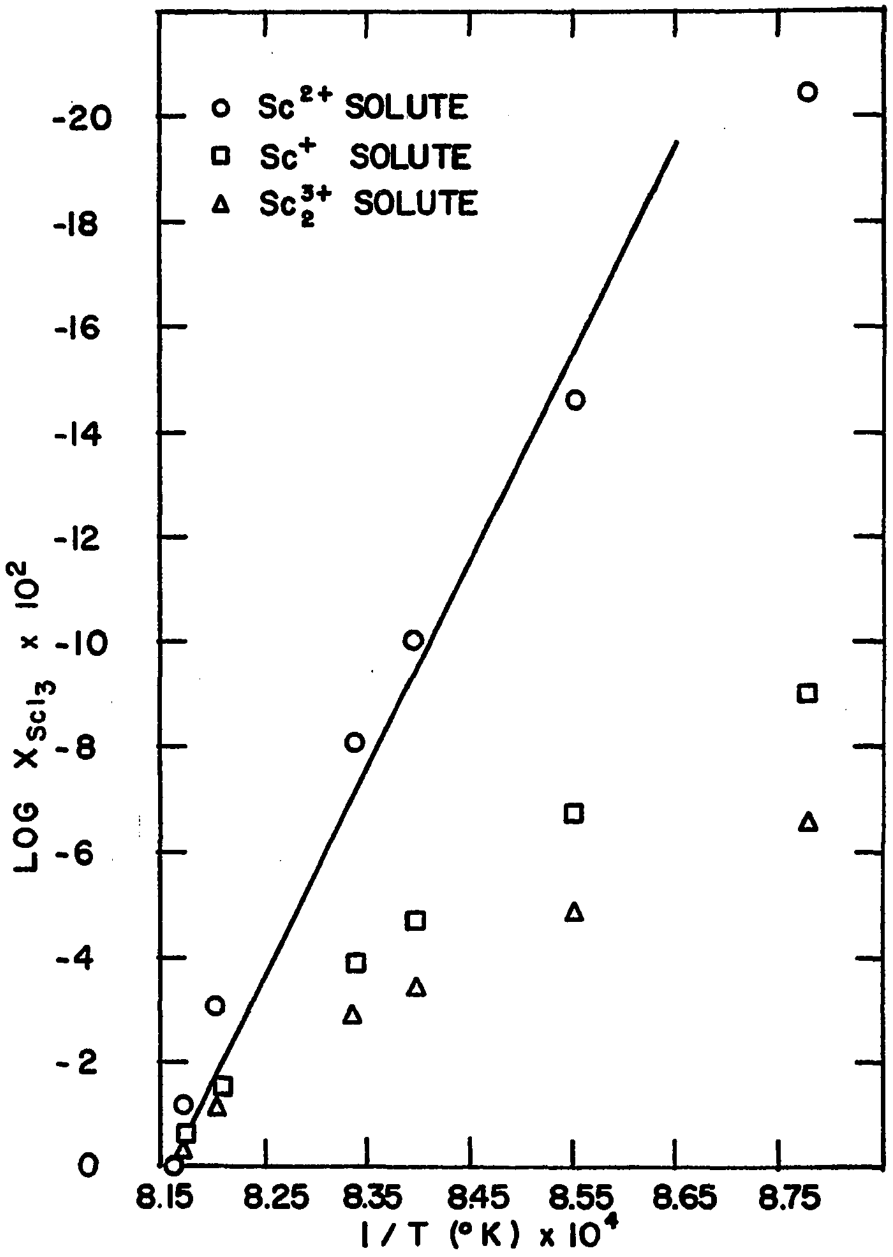


Figure 6. Cryoscopic data for the solution of Sc in ScI_3

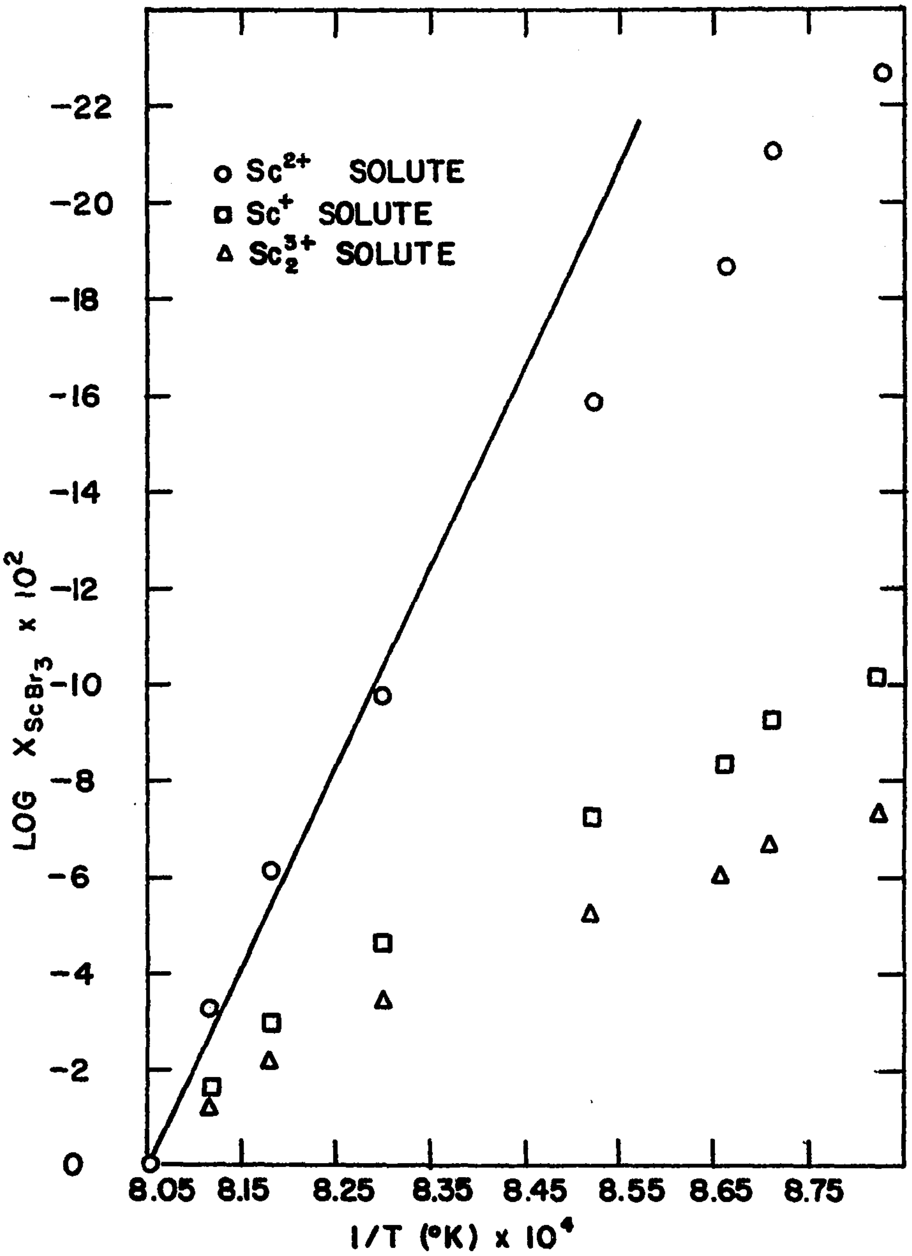


Figure 7. Cryoscopic data for the solution of Sc in $ScBr_3$

systems, respectively.

Using the freezing point depression data obtained for the phase diagrams, the mole fractions of solvent corresponding to the quantities of Sc metal used were calculated for each of the following solution processes where the associated anions were iodide or bromide.

$$2\ Sc^{3+} + Sc = 3\ Sc^{2+}$$

$$Sc^{3+} + Sc = Sc_2^{3+}$$

$$Sc^{3+} + 2\ Sc = 3\ Sc^{+}$$

In Figures 6 and 7 are shown the fit for the various solute models with the slope obtained using Brewer's enthalpy of fusion for the scandium trihalide. It is apparent that the data corresponding to the formation of Sc^{2+} provide the best fit over the solution range used in both systems. It should be noted that the data agreed rather well even at about 10 mole % Sc where the mole fraction of Sc^{2+} in the trihalide was up to about 0.3 ($\log X$ solvent $= -15.4 \times 10^{-2}$). This has extensive precedent in various rare earth metal halide systems, especially in the $NdCl_3$-Nd and $DyCl_3$-Dy systems where divalent salts were formed as established by Corbett and co-workers (12, 13). It is interesting to note the similar behavior of the two systems in fairly dilute solution, despite the considerable behavioral contrasts of the subhalides formed. Similar behavior is noted for dilute solutions of the light rare earth metals in their molten chlorides and iodides. The specific conductivities of these dilute solutions have been investigated by Bredig and co-workers (48-51) who found that dilute solutions of metals in their chlorides and iodides have similar specific conductivities with rather large electronic contributions consistent with the possible equilibrium $M^{2+} = M^{3+} + (e)^-$ in which the electron was considered to occupy an anionic site vacancy. Certainly no long range conduction band was formed since the temperature coefficient for the conductivity was positive in every case. Cryoscopically, the solvated electron was thought possibly to be indistinguishable from the M^{2+} ion (the M^{3+} ion formed being common to the solvent). Additional evidence of the feasibility of the above equilibrium was that as the stability of M^{2+} increased ($Nd^{2+} > Pr^{2+} > Ce^{2+} \sim La^{2+}$), the conductivity was properly observed to decrease. Thus, from the resistivity data on the solid scandium subiodide and the expected similar thermodynamic stability of scandium dihalide with that of Pr, it is likely that the conductivity of dilute solutions for the scandium halides would be very much like the corresponding praseodymium samples.

The deviations from the calculated slope for the most dilute melts, which were most pronounced for the iodide system, are consistent with solid solution formation. This has been indicated by the dashed lines in the ScI_3-Sc phase diagram. A recent value of the enthalpy of fusion of $ScCl_3$ of 16.1 kcal./mole[1] is some 3 kcal./mole less than that used for $ScBr_3$ which should be comparable. Presuming the value for ScI_3 used was similarly high, the deviations for the most dilute solutions from the calculated slopes for both systems would be somewhat more pronounced than shown.

Magnetic data for $ScBr_{1.5}$

The resistance of a manually pressed pellet of $ScBr_{1.5}$ was about one megohm across 1/4 inch of sample. Presuming this to imply the presence of localized electrons, magnetic data for $ScBr_{1.5}$ were obtained using a Faraday balance. When these data were taken, difficulties with the temperature measuring equipment forced the use of suitable slush baths. The data, which are found in the Appendix, are shown in Figure 8 as $1/\chi_M$ versus T, where χ_M is the molar susceptibility corrected for the diamagnetism of the sample and extrapolated to infinite field by the Honda-Owen method. No unusual field dependence was observed and significant magnetic impurities were thought unlikely.

The magnetic susceptibility varied rather smoothly from 81×10^{-6} emu./mole at room temperature to 125×10^{-6} emu./

---

[1] A. S. Dworkin and M. A. Bredig, The Oak Ridge National Laboratory, Oak Ridge, Tennessee. The enthalpy of fusion of $ScCl_3$. Private communication. 1969.

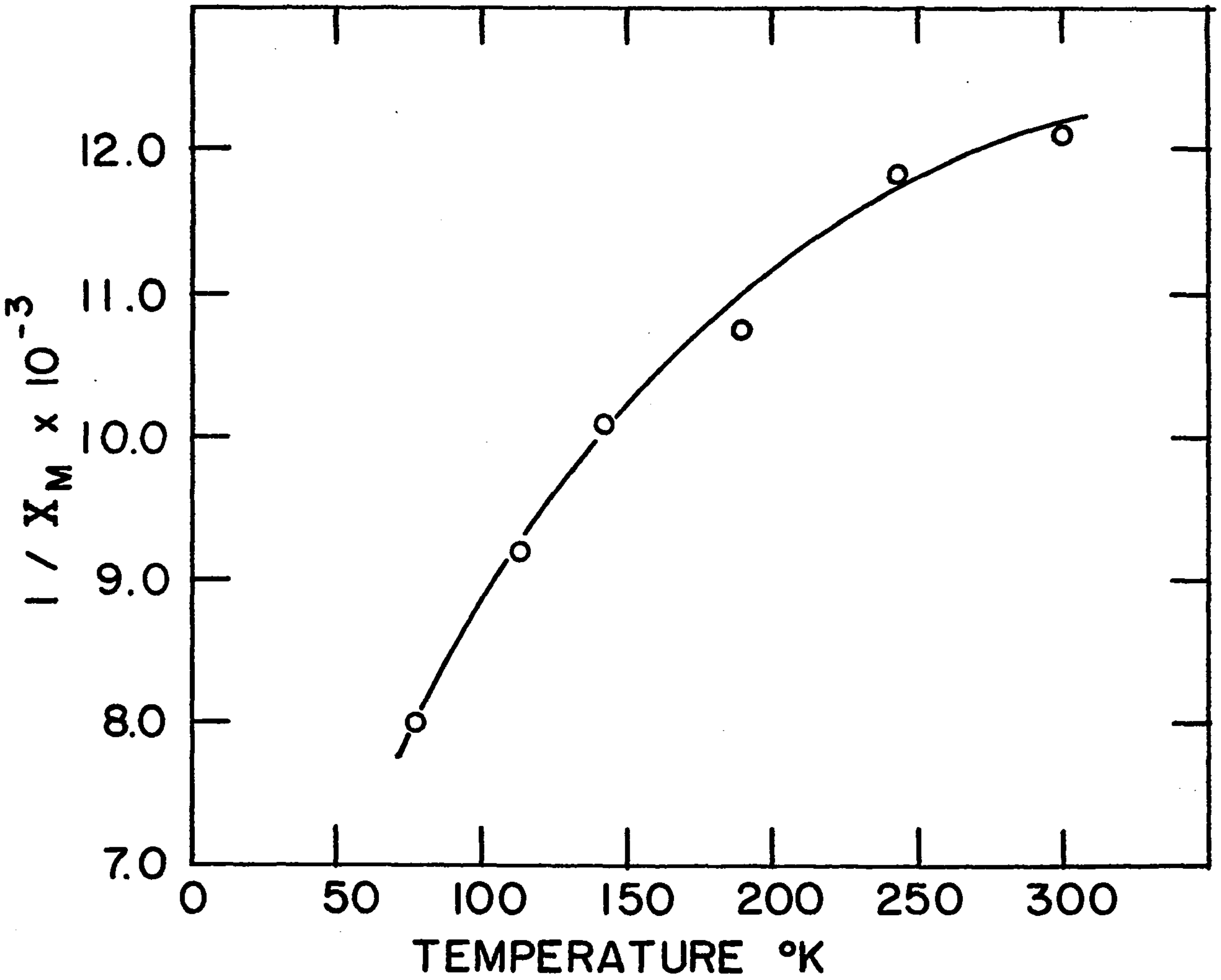


Figure 8. The temperature dependence of the molar magnetic susceptibility of $ScBr_{1.5}$

mole at 77° K. Since the paramagnetic molar susceptibility was only slightly greater than the sample diamagnetism, some scatter was unavoidable because of the very small weight changes recorded for the sample in the magnetic field. The sample was very slightly paramagnetic and somewhat temperature dependent. Assuming Curie law obedience, the magnetic moment, u_{eff}, at room temperature was calculated to be about 0.44 β.

Preparation of $ScCl_{1.5}$

After the $ScBr_3$-Sc phase diagram had been determined, it was noticed that it had some features in common with the $ScCl_3$-Sc diagram reported by Polyachenok and Novikov, particularly a peritectic at about 880° (18). Although their $ScCl_3$ was no doubt inferior to that of Corbett and Ramsey (16), it was recalled that in the early part of the investigation of the ScI_3-Sc system the author used some mistakenly labeled "as reduced" Sc metal. This metal was later found to contain up to 3% Mg, and it inhibited the formation of the scandium subiodide. If Corbett and Ramsey had also mistakenly used this metal, for additions to $ScCl_3$, an incorrect phase diagram could have resulted. Since some $ScCl_3$ still remained from that work, this was resublimed in tantalum and equilibrated with excess scandium at 860°. The result was that a new phase visually identical to $ScBr_{1.5}$ was formed. The powder patterns of the two materials were similar, and considering the differences in the diffracting ability of Br and Cl nuclei, they are probably isostructural. The powder patterns of $ScBr_{1.5}$ and $ScCl_{1.5}$ are in the Appendix. An analysis of one sample gave a stoichiometry of $ScCl_{1.46}$, but this was a rather impure sample as indicated by a poor material recovery of 98.6%. As was usual, some insoluble material was present so that the analysis was somewhat better than that. No phase diagram work was performed since very little $ScCl_3$ remained, and little time was available to devote to its redetermination.

Attempts to obtain single crystals of $ScBr_{1.5}$

The powder diffraction patterns of $ScBr_{1.5}$ and $ScCl_{1.5}$ were always of poor quality. The best of these were taken of small fibers of $ScBr_{1.5}$ pulled from the matted sample. Attempts to grind the material to a powder proved rather futile because the sample "caked" badly. Long grinding would produce a fairly finely divided product, but these gave diffraction patterns of unimproved quality. Since structural information about $ScBr_{1.5}$ was obviously needed to rationalize its formation, attempts were made to get crystals of sufficient quality to at least determine lattice parameters.

While dissolving samples of $ScBr_{1.5}$ for analysis in absolute ethanol, it was noticed that very small needles seemed to be the last to dissolve. Thus, attempts were made to obtain single crystals from well annealed $ScBr_{1.5}$ by partially dissolving the sample, pouring off most of the excess solvent, and quickly pumping off the last traces of solvent. Absolute ethanol, propylene carbonate, acetonitrile, and acetone were tried as solvents. Ethanol reacted too vigorously, propylene carbonate too slowly, if at all, and acetonitrile gradually gave a yellow product that coated any remaining material. Acetone seemed to offer the best possibility, and the technique seemed to work, but no single crystals were forthcoming. The best results, small "crystals" which turned out to be fibrous bundles, were produced from material annealed at 800°. Efforts were made to grow small amounts of $ScBr_{1.5}$ at 550°, 630°, and 680° by equilibration of pieces of Sc metal with small quantities of $ScBr_3$. The reaction was incomplete at the lower two temperatures and at 680° gave a thin layer of apparently non-crystalline product which adhered to the metal.

In an attempt to achieve better nucleation of $ScBr_{1.5}$, a sample of $ScBr_3$ + excess metal was equilibrated well above the peritectic and then slowly cooled at a rate no greater than 1° or 2° every two hours over the range of 10° above and below the peritectic temperature. It was subsequently cooled at a somewhat faster rate to 700°, and then more rapidly to room temperature. The product was no better than before. Use of strips of metal sheet for equilibration also failed to give good results.

Attempts were made to recrystallize $ScBr_{1.5}$ from both molten $KAlBr_4$ and a molten KBr-NaBr eutectic composition. $ScBr_{1.5}$ apparently failed to dissolve in $KAlBr_4$. Using the KBr-NaBr eutectic mixture, a small amount of $ScBr_{1.5}$ was heated in a tantalum container at 800° and slowly cooled through the eutectic temperature of 640°. Most of the material was only slightly discolored, but some dark-colored crystalline-appearing material resulted which was in a cubic matrix and which certainly was not $ScBr_{1.5}$. From this and the other experiments, it was concluded that, though single crystals of $ScBr_{1.5}$ may be obtainable, considerable patience might be required in getting them.

Discussion of $ScCl_{1.5}$ and $ScBr_{1.5}$

Because of the paucity of experimental results, any discussion of these compounds must be conjectural. The compositions seem fairly well established, and $ScBr_{1.5}$ appears to be an electrical insulator which exhibits a weakly temperature dependent paramagnetism. The compounds are identical in appearance and probably are isostructural, based on their X-ray diffraction patterns. They are very air sensitive and oxygen contamination was a problem in their preparation. Crystals of these materials form poorly. Very small, almost microscopic, crystals appear acicular; somewhat larger "crystals" tend to occur as bundles of the smaller crystals. Although some guesses may be made about the nature of these compounds, an X-ray structural determination is obviously needed.

The obvious choice for comparison with $ScCl_{1.5}$ or $ScBr_{1.5}$ is the compound of reported stoichiometry $GdCl_{1.6}$. Additionally, the halides of these metals might be compared because both form subiodides which appear to be metallic conductors (11). Crystals of the gadolinium chloride tend to split easily along their needle axis resulting in a "frayed rope" appearance which might be compared to the crystalline bundles found for $ScBr_{1.5}$. Recently, X-ray structural work on single crystals has shown the true stoichiometry is $GdCl_{1.50}$ and that metal-metal interactions are certain from the interatomic distances.[1] From this, considering the f^7 core for Gd to be chemically inert, $GdCl_{1.5}$, $ScCl_{1.5}$, and $ScBr_{1.5}$ all exhibit 1.5 valence electrons per metal atom. Magnetic data for $GdCl_{1.5}$ has been found to correlate very well with the assumption of a $4f^7$-electron core, with the remaining metal electrons contributing very little to the total magnetic moment (15), and any greatly reduced magnetic moment from metal-metal interactions comparable to the moment observed for $ScBr_{1.5}$ would have been effectively masked by the very high contribution from the f^7 core. To sum up, reasons of stoichiometry, possible magnetic

---

[1] D. A. Lokken, Ames Laboratory of the United States Atomic Energy Commission, Iowa State University of Science and Technology, Ames, Iowa. Data from the structural determination of $GdCl_{1.5}$. Private communication. 1969.

similarities, and the conductivity of the subiodides of both metals suggest that structural similarities may exist. Some differences are apparent. It is not thought that either the subchlorides or subiodides of the two metals are isostructural. Second, the $GdCl_{1.5}$ melts incongruently some 250° lower than $ScBr_{1.5}$. Third, the scandium subiodide appears to exist only in nonstoichiometric form; the GdI_2, though not certain to be stoichiometric, appears to be nearly so. Several fortuitous effects may help explain some of the similar properties of these materials. A high third ionization potential for scandium helps to stabilize lower valence states with respect to disproportionation while lower valence states (or bands) enjoy no such advantage with gadolinium. The 5d-orbitals of Gd extend much further than the 3d-orbitals of Sc (though the 3d extension maximum is at scandium) which should allow increased stabilization by metal-metal interaction. Similar considerations are probably appropriate at yttrium, which forms no subhalides, and lanthanum, which forms two subiodides but no subchloride. Lanthanum has the greatest 5d radial extension among the rare earth elements and may fail to form a subchloride chiefly because its third ionization is about 15 kcal./mole lower than that of gadolinium (9).

Although comparison of $ScCl_{1.5}$ and $ScBr_{1.5}$ with $GdCl_{1.5}$ seems appropriate, possibilities for the scandium compounds range from ionic materials composed of cations of mixed valence states to covalent materials exhibiting considerable metal-metal interactions as has been suggested above. Those compounds of the first sort usually involve metals which exhibit two or more comparably stable cationic oxidation states. For scandium, the trivalent state certainly dominates, and the divalent state should be the next most stable according to the thermodynamic arguments presented in the introductory section. It is difficult to believe that Sc(I) can exist as such, and if it did, it would be paramagnetic, presuming the d^1s^1 configuration to be more stable than s^2 as has been reported in the gaseous state (52). It might still be possible to formulate $ScBr_{1.5}$ as something like $[Sc(I)]_3$ $[Sc(III)Br_6]$ as was suggested for In_2Cl_3 and In_2Br_3 by Kleinberg and co-workers (53, 54), although the very low melting points of these compounds (~ 230°) suggest that any comparison would be tenuous. This formulation was unsubstantiated, moreover, and it now seems likely that for the bromide, at least, the composition should be $InBr_{1.4}$ with a very large unit cell (55, 56).

Other cluster formulations are also possible, including formation of a simple dimer such as Sc_2^{3+} or larger units including halogen atoms such as are well known for 4d and 5d metal halides. An objection to this might be that radial extensions of the scandium d-orbitals would not provide sufficiently strong metal-metal interactions and that such species might have been expected to be either diamagnetic or more paramagnetic than was observed.

FUTURE WORK

Although the existence of the scandium subiodide phase has been established, and some indications for solid solution in this phase have been reported, the extent and temperature dependence of solid solution have not been established. Further study might prove useful if quenching of samples from high equilibration temperatures is effective. The region of solid solution might be only roughly outlined by examination of X-ray powder photographs, because the presence of perhaps 10% ScI_3 would be necessary for its detection. A suspected slight change in the cell parameters of the subiodide with composition could be followed if good quality X-ray Guinier powder data were taken. The process of grinding samples often serves to broaden lines so that further equilibration of the finely powdered samples may be necessary. These techniques could also be applied to samples of the approximate composition $ScI_{2.5}$ and perhaps ScI_3 to try to establish the source of the weak lines observed in several intermediate compositions.

Several interesting possibilities for future work are suggested by the results obtained from the ScI_3-Sc system. These involve investigation of the physical properties of the scandium subiodide and related iodides. The observation of rather subtle changes in the X-ray powder diffraction data in samples of different composition and the apparent lack of correlations between the magnetic data for the composition $ScI_{2.15}$ and the resistivity data for the composition $ScI_{2.23}$ suggest that these data may be composition dependent. Both magnetic and resistivity data should be taken at several compositions, say $ScI_{2.25}$ and $ScI_{2.15}$, to check this. Magnetic data at these compositions, preferably down to liquid helium temperature, should be easily obtainable. The technique used here for resistivity measurements should be abandoned because of the general difficulties reported earlier, and the preparation of homogeneous rods of desired compositions (especially fully-reduced samples) may be impossible. Since it is a simple matter to produce powdered samples of desired compositions, the resistivity measurements at various temperatures should be made using an inductance technique.

The observations that at least one form of TiI_2 appears to exhibit substantial electrical conductivity and that VI_2 is probably an intrinsic semiconductor very likely relate the behavior of the scandium subiodide to these materials as well as to the various metallic rare earth diiodides. These and other early transition metal halides might prove of more general interest to solid state physicists if they were available in pure forms and further magnetic and some conductivity data were available. Thus, if the techniques suggested earlier for the preparation of the two forms of TiI_2

prove successful, the more complete investigation of their magnetic properties would be useful, especially if one or both forms should be found to be metallic conductors.

After the above experiments, attention might be paid to the transitions observed in the magnetic and resistivity data for the scandium subiodide. For the early transition metal oxides, magnetic ordering and transitions in the conductivity (often metal-semiconductor transitions) may be associated with crystalline distortion or magnetic ordering or both. (A recent review by Adler (57) serves as a good introduction to the physical properties of transition metal oxides and the pertinent literature.) Although a crystalline change may not be associated with the magnetic or resistivity transitions in the scandium subiodide, this seems possible, and low temperature X-ray powder work, preferably using Guinier cameras for greater sensitivity, would be a useful routine check for crystalline changes with temperature on the subiodide and other samples exhibiting anomalous magnetic and conductivity transitions. Of course, speculation on the need for investigations of the nature of magnetic and conductivity transitions in the scandium subiodide may be premature since further work in both these areas is needed.

Some additional work also appears appropriate for the scandium chloride and bromide systems. Several thermal analysis runs for the $ScCl_3$-Sc should serve to establish the shape of the liquidus beyond the eutectic, the peritectic composition, and melting point of $ScCl_{1.5}$. Very careful work should better establish whether the stoichiometries $ScCl_{1.5}$ and $ScBr_{1.5}$ are exactly as indicated. Structural information on one of these compounds is needed but this depends on the availability of single crystals of either material. It is doubtful that magnetic data for $ScCl_{1.5}$ would be more informative than that obtained for $ScBr_{1.5}$.

BIBLIOGRAPHY

1. E. A. Ukshe and N. G. Bukun, Russ. Chem. Rev., 30, 90 (1961).
2. Yu. K. Delimarskii and B. F. Markov, "Electrochemistry of Fused Salts," The Sigma Press, Washington, D.C. 1961.
3. L. B. Asprey and B. B. Cunningham, Prog. Inorg. Chem., 2, 267 (1960).
4. J. D. Corbett, "The Solution of Metals in Their Molten Salts," in B. R. Sundheim, ed., "Fused Salts," McGraw-Hill, New York, N.Y. 1964.
5. M. A. Bredig, "Mixtures of Metals with Molten Salts," in M. Blander, ed., "Molten Salt Chemistry," Interscience Publishers, New York, N.Y. 1964.
6. J. D. Corbett, D. L. Pollard, and J. E. Mee, Inorg. Chem., 5, 761 (1966).
7. C. E. Habermann and A. H. Daane, J. Chem. Physics, 41, 2818 (1964).
8. D. A. Johnson and J. D. Corbett, Les comptes-rendes de la Colloque internationeaux du CNRS, les Elementes des terres rares, Paris. *ca.* 1970. In press.
9. D. A. Johnson, J. Chem. Soc., A, 1525 (1969).
10. J. D. Corbett, L. F. Druding, W. J. Burkhard, and C. B. Lindahl, Disc. Faraday Soc., 32, 79 (1962).
11. J. E. Mee and J. D. Corbett, Inorg. Chem., 4, 88 (1965).
12. L. F. Druding and J. D. Corbett, J. Amer. Chem. Soc., 83, 2462 (1961).
13. J. D. Corbett and B. C. McCollum, Inorg. Chem., 5, 938 (1966).
14. P. Caro and J. D. Corbett, J. Less-Common Metals, 18, 1 (1969).
15. J. D. Greiner, J. F. Smith, J. D. Corbett, and F. J. Jellinek, J. Inorg. Nucl. Chem., 28, 971 (1966).

16. J. D. Corbett and B. N. Ramsey, Inorg. Chem., 4, 260 (1965).

17. M. Barber, J. W. Linnett, and N. H. Taylor, J. Chem. Soc., 3323 (1961).

18. O. G. Polyachenok and G. I. Novikov, Zh. Neorg. Khim., 8, 2819 (1963).

19. O. G. Polyachenok and G. I. Novikov, Russ. Chem. Rev., 33, 342 (1964).

20. P. G. Nelson and A. G. Sharpe, J. Chem. Soc., A, 501 (1966).

21. J. P. Dismukes and J. G. White, Inorg. Chem., 3, 1220 (1964).

22. J. C. McGuire and C. P. Kempter, J. Chem. Physics, 33, 1584 (1960).

23. F. Petru and V. Dufek, Z. Chem., 6, 345 (1966).

24. D. Brown, "Halides of the Lanthanides and Actinides," J. Wiley and Sons, New York, N.Y. 1968.

25. L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, "The Thermodynamic Properties of the Halides," in L. L. Quill, ed., "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," Pp. 76-193, McGraw-Hill, New York, N.Y. 1950.

26. F. H. Spedding and A. H. Daane, Metallurgical Rev., 5, 297 (1960).

27. J. Korbl and R. Pribil, Chemist-Analyst, 45, 102 (1956).

28. B. C. McCollum, "A Phase Study of the Dysprosium-Dysprosium(III) Chloride System," unpublished M.S. thesis, Library, Iowa State University of Science and Technology, Ames Iowa. 1965.

29. J. E. Mee, "Metal-Metal Halide Systems of Gadolinium and Yttrium," unpublished Ph.D. thesis, Library, Iowa State University of Science and Technology, Ames, Iowa. 1962.

30. J. D. Corbett, R. A. Sallach, and D. A. Lokken, Advan. Chem. Series, 71, 56 (1967).

31. J. G. Converse, "Magnetic and Spectral Characterization of Some Group V B and VI B Transition Metal Halide Complexes," unpublished Ph.D. thesis, Library, Iowa State University of Science and Technology, Ames, Iowa. 1968.

32. R. J. Clark and J. D. Corbett, Inorg. Chem., 2, 460 (1963).

33. R. A. Sallach, "Electrical Resistivities and Magnetic Susceptibilities of Some Rare Earth Metal-Metal Halide Systems," unpublished Ph.D. thesis, Library, Iowa State University of Science and Technology, Ames, Iowa. 1963.

34. P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N.Y. 1956.

35. T. Tsuchida and W. E. Wallace, J. Chem. Physics, 43, 2885 (1965).

36. G. A. Samara and H. G. Drickamer, J. Chem. Physics, 37, 408 (1962).

37. C. Kittel, "Introduction to Solid State Physics," J. Wiley and Sons, New York, N.Y. 1956.

38. J. B. Mann, "Atomic Structure Calculation II. Hartree-Fock Wavefunctions and Radial Expectation Values," AEC Report LA-3691, Los Alamos Scientific Laboratory, 1968.

39. W. Klemm and L. Grimm, Z. Anorg. Allg. Chem., 249, 209 (1942).

40. D. Juza, D. Giegling, and H. Schäfer, Z. Anorg. Allg. Chem., 366, 121 (1969).

41. W. Klemm, E. Holze, and W. Basualdo, Congr. intern. chim. pure et appl., 16^{e}, Paris, 1957. Mem. sect. chim. minerale, pp. 43-46. 1957.

42. J. D. Fast, Rec. Trav. Chim., 58, 174 (1939).

43. R. F. Rolsten and H. H. Sisler, J. Amer. Chem. Soc., 79, 5891 (1957).

44. A. Herzog and L. M. Pidgeon, Can. J. Chem., 34, 1687 (1956).

45. K. Funaki, K. Uchimura, and H. Matsunaga, Kogyo Kagaku Zasshi, 64, 129 (1961).

46. W. Klemm and L. Grimm, Z. Anorg. Allg. Chem., 249, 198 (1942).

47. K. O. Berry, R. R. Smardzewskii, and R. E. McCarley, Inorg. Chem., 8, 1994 (1969).

48. A. S. Dworkin, R. A. Sallach, H. R. Bronstein, M. A. Bredig, and J. D. Corbett, J. Phys. Chem., 67, 1145 (1963).

49. H. R. Bronstein, A. S. Dworkin, and M. A. Bredig, J. Phys. Chem., 66, 44 (1962).

50. A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, Disc. Faraday Soc., 32, 188 (1961).

51. A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, J. Phys. Chem., 66, 1201 (1962).

52. C. E. Moore, National Bureau of Standards Circulars 467-1 (1949); 467-2 (1952); 467-3 (1958), U.S. Government Printing Office, Washington, D.C.

53. R. J. Clark, E. Griswold, and J. Kleinberg, J. Amer. Chem. Soc., 80, 4764 (1958).

54. P. H. Walter, J. Kleinberg, and E. Griswold, J. Inorg. Nucl. Chem., 19, 223 (1961).

55. W. Morawietz, H. Morawietz, and G. Brauer, Z. Anorg. Allg. Chem., 316, 220 (1962).

56. G. Brauer and H. Morawietz, Z. Anorg. Allg. Chem., 340, 133 (1965).

57. D. Adler, Rev. Modern Phys., 40, 714 (1968).

ACKNOWLEDGMENTS

The author wishes to thank Dr. John D. Corbett for his guidance, encouragement, and patience during the course of this work.

He also wishes to thank Dr. F. H. Spedding for the scandium metal used in this work, Dr. R. E. McCarley for the use of his Faraday balance and Jim Converse and Jim Hamilton for their help with the details of its use, John Croat for cleaning the tantalum used by induction heating, and Norm Linder for the construction of many tantalum containers by the electron-beam welding technique.

The author wishes to thank members of Physical and Inorganic Group Nine for their discussion, advice, and cooperation regarding this research. As important as any of the above, he wishes to thank his friends at Iowa State for helping to make his stay in Ames bearable.

APPENDIX

Table 1. Thermal analysis data for the ScI_3-Sc phase diagram

Run #	Mole % Sc in ScI_3	Thermal arrests (° C)	
5	0	948	-[a]
	23.31	885	-[a]
	28.60	894	
	31.67	893	
	35.10	892	
9	3.41	939	
	8.28	902.5	839[b]
	11.05	867	846.5
	17.53	856.5	847
	22.60	883	-[a]
	25.11	891	
10	0	951	
	5.65	926	
	14.35	849	845.5
	20.50	872	-[a]
	28.92	891	
11	0	952	
	0.87	950.5	
	2.25	946	
	6.85	918.5	
	9.50	896	
	12.50	866	847
	16.00	847	
	19.20	860.5	

[a] The dash indicates that only one thermal effect was observed.

[b] The thermal effect was very weak.

Table 2. Equilibration data used in the ScI_3-Sc phase diagram

Eq. #	Time	Temp. ° C	Analysis (mole % Sc)	Weight recovery (%)
5	25 hrs	909	24.85	-
6	25 hrs	931	25.01	99.7
7	3.0 days	885	28.65	99.9+
10	21 hrs	974	24.78	99.9+
11	7 days	886	27.87	99.3
12	21 days	870	28.08	99.8
13	14 days	870	29.14	99.3
14	4.5 days	869	28.26	100.0
15	17.5 hrs	947.5	24.94	100.4
16	7 days	872	28.16	100.0
18	12 days	869	28.38	100.0

Table 3. Thermal analysis data for the $ScBr_3$-Sc phase diagram

			Thermal arrests ($^\circ$ C)	
Run #	Mole % Sc in $ScBr_3$	col 1	col 2[a]	col 3
1	0	968.5	850	-
	6.71	932		818.5
	13.90	861		821
	19.37	816.5		
	22.69	868		818
	24.55	880.5		819.5
	27.46	880.5		819
2	0	968.5		-
	2.40	959		
	4.38	949.5		
	10.20	900.5	851	
	12.81	875	851	817
	15.61	845		818
	19.50	816.5		
	20.79	831.5		816
	21.75	848		816
3	0	970		-
	11.65	881.5		817
	14.85	849		817
	16.25	841		818
	17.18	834.5		817.5
	18.34	824		817
	20.95	822.5		815.5

[a] Those thermal arrests shown in column 2 were very weak and only discovered by careful re-examination of the thermal analysis charts after the change in slope of the liquidus at 15 mole % Sc and 850° C was observed.

Table 4. Equilibration data used in the $ScBr_3$-Sc phase diagram

Eq. #	Time	Temp. (° C)	Analysis (mole % Sc)	Weight recovery (%)
1	13 hrs	980	24.14	99.6
2	17 hrs	899	25.14	99.4
3	33 hrs	863	47.19	97.3
4.1[a]	1 day	990		
	7 days	863	42.2	99.4
4.2[b]	3 days	865		
4.3[c]	7 days	860	50.11	97.3
5	22.5 hrs	959.5	23.78	99.5
6[c]	16 hrs	1006	27.30	98.4
7	22 hrs	927.5	22.59	99.9
8.3[d]		860	50.53	98.7
9[e]	21 hrs	1041	24.13	
10[e]	19 hrs	903	23.00	

[a] One-half of the sample was analyzed.

[b] This sample was not analyzed; just a small portion for an X-ray diffraction pattern was removed.

[c] This sample was accidentally heated at above 1100° for several hours prior to equilibration at 1006°. Further, small crystals of material later identified as ScOBr were found in the sample.

[d] Result of three successive equilibrations of 3 to 7 days each.

[e] Several pieces of Sc metal were removed from the product and a meaningful weight check was not obtained.

Table 5. Resistance data for $ScI_{2.23}$

Bath	T (°K)	Frequency (cps)	I^a (ma)
None	299	100	300
		300	300
		500	300
		100	500
		300	500
		500	500
		100	750
		300	750
		500	750
Hot water	355	100	300
		300	300
		500	300
		100	500
		300	500
		500	500
		100	750
		300	750
		500	750
Warm water	324	100	300
		300	300
		500	300
		100	500
		300	500
		500	500
		100	750
		300	750
		500	750
NaCl-ice slush	265	100	300
		300	300
		500	300
		100	500
		300	500

---

[a] The value listed for I (current) was approximate.

[b] The value of the standard resistor was 0.05989 ohms.

V (std)[b] (volts)	V (sample) (volts)	R (sample) x 10^3 (ohms)
1.60	0.132	4.94
1.91	0.157	4.92
1.87	0.154	4.93
2.45	0.200	4.89
2.96	0.242	4.90
2.90	0.240	4.96
4.20	0.345	4.92
5.01	0.415	4.96
5.00	0.410	4.91
1.47	0.153	6.21
1.77	0.183	6.19
1.76	0.184	6.26
2.495	0.247	6.10
2.89	0.297	6.15
2.86	0.295	6.18
4.50	0.460	6.12
5.45	0.550	6.04
5.40	0.545	6.04
1.46	0.131	5.37
1.76	0.161	5.48
1.74	0.164	5.64
2.48	0.221	5.34
2.99	0.266	5.33
2.95	0.266	5.40
4.40	0.394	5.36
5.30	0.473	5.34
5.24	0.470	5.37
1.56	0.105	4.03
1.87	0.127	4.07
1.85	0.127	4.11
2.47	0.167	4.05
2.98	0.201	4.04

Table 5. (Continued)

Bath	T (° K)	Frequency (cps)	I^a (ma)
NaCl-ice slush cont.		500	500
		100	750
		300	750
		500	750
CCl_4 slush	252	100	300
		300	300
		500	300
		100	500
		300	500
		500	500
		100	750
		300	750
		500	750
Diethyl malonate slush	222	100	300
		300	300
		500	300
		100	500
		300	500
		500	500
		100	750
		300	750
		500	750
Dry Ice-acetone slush	192.5	100	300
		300	300
		500	300
		100	500
		300	500
		500	500
		100	750
		300	750
		500	750

V (std)[b] (volts)	V (sample) (volts)	R (sample) x 10^3 (ohms)
2.94	0.200	4.07
4.44	0.300	4.05
5.34	0.360	4.04
5.28	0.358	4.06
1.49	0.095	3.82
1.80	0.116	3.86
1.77	0.118	3.99
2.51	0.159	3.79
3.00	0.193	3.85
2.96	0.192	3.88
4.50	0.315	4.19
5.40	0.380	4.21
5.35	0.380	4.25
1.47	0.097	3.95
1.77	0.117	3.96
1.76	0.118	4.02
2.43	0.146	3.60
2.91	0.173	3.56
2.87	0.172	3.59
4.60	0.274	3.57
5.50	0.328	3.57
5.43	0.323	3.56
1.51	0.106	4.20
1.80	0.129	4.29
1.77	0.125	4.23
2.42	0.171	4.23
2.91	0.206	4.24
2.88	0.206	4.28
4.60	0.323	4.21
5.52	0.390	4.22
5.45	0.380	4.18

Table 5. (Continued)

Bath	T (°K)	Frequency (cps)	I[a] (ma)
n-pentane slush	160	100	300
		300	300
		500	300
		100	500
		300	500
		500	500
		100	750
		300	750
		500	750

V (std)[b] (volts)	V (sample) (volts)	R (sample) x 10^3 (ohms)
1.57	0.109	4.15
1.89	0.132	4.18
1.85	0.134	4.34
2.50	0.177	4.24
2.96	0.215	4.35
2.87	0.214	4.47
4.55	0.313	4.12
5.40	0.387	4.29
5.38	0.382	4.25

Table 6. Resistivity data on $ScI_{2.23}$[a]

T ($^\circ$ K)	R (ohms) x 10^3	ρ (ohm cm) x 10^3
160	4.35	1.09
192.5	4.24	1.06
222	3.56	0.89
252	3.85	0.96
265	4.04	1.01
299	4.90	1.22
324	5.33	1.33
355	6.15	1.54

[a] From data taken at 500 ma. and 300 cps and used in Figure 3. For complete data see Table 5 in the Appendix.

Table 7. Magnetic data for $ScI_{2.15}$

T (^{o}K)	1/T x 10^3 (^{o} K^{-1})	χ_g x 10^6 (emu/g)	χ_M x 10^6 (emu/mole)	χ_M (corr)[a] x 10^6 (emu/mole)	1/χ_M (corr) x 10^{-3} (mole/emu)
299	3.34	0.744	237.4	359.4	278.2
331	3.02	0.724	230.9	352.9	283.4
345	2.90	0.727	231.8	353.8	282.6
77	13.00	1.187	378.7	500.7	199.7
77	13.00	1.180	376.6	498.6	200.6
113	8.85	1.263	403.1	525.1	190.4
118	8.48	1.317	420.1	542.2	184.4
120	8.33	1.309	417.8	539.2	185.5
125	8.00	1.295	413.1	535.2	186.8
131	7.63	1.276	407.2	529.2	189.0
145	6.90	1.209	385.9	507.9	196.9
162	6.17	1.145	365.4	487.4	205.2

---

[a] Corrected for χ_D of the sample; χ_D = -122 x 10^{-6} emu/mole.

Table 7. (Continued)

T (°K)	1/T x 10^3 (° K-1)	χ_g x 10^6 (emu/g)	χ_M x 10^6 (emu/mole)	χ_M (corr)[a] x 10^6 (emu/mole)	1/χ_M (corr) x 10^{-3} (mole/emu)
184	5.44	1.093	348.7	460.7	217.1
195	5.13	1.041	332.2	454.2	220.2
206	4.85	1.000	319.0	441.0	226.8
230	4.35	0.898	286.5	408.5	244.8
260	3.85	0.764	243.7	365.7	273.4
298	3.36	0.742	236.8	358.6	278.9
78	12.8	1.184	378	500	200.0
85	11.8	1.160	370	492	203.3
89	11.2	1.134	362	484	206.6
93	10.7	1.115	356	478	209.2
98	10.2	1.110	354	476	210.1
103	9.70	1.102	352	474	211.0
110	9.08	1.175	375	497	201.2
112	8.92	1.254	400	522	191.6

Table 8. Magnetic data for $ScBr_{1.5}$

T ($^{\circ}$ K)	$1/T \times 10^3$ ($^{\circ}$ K^{-1})	$\chi_g \times 10^6$ (emu/g)	$\chi_M \times 10^6$ (emu/mole)	χ_M (corr)[a] $\times 10^6$ (emu/mole)	$1/\chi_M$ (corr) $\times 10^{-3}$ (mole/emu)
77	10.30	0.384	63.2	125.2	7.98
113	8.85	0.284	46.9	108.9	9.18
142	7.04	0.226	37.2	99.2	10.09
189	5.29	0.190	31.3	93.3	10.73
242	4.13	0.137	22.5	84.5	11.84
299	3.35	0.114	18.7	80.7	12.11

[a] Corrected for χ_D of the sample; $\chi_D = -62 \times 10^{-6}$ emu/mole.

Table 9. X-ray powder diffraction data for ScI_3

Lattice constants: $a_o = 4.125$ Å; $c_o = 6.805$ Å

θ (for Cu Kα)	d (obs) Å	d (calc) Å	hkl	Intensity
6.50	6.8	6.805	001	20
12.46	3.57	3.572	100	15
13.13	3.39	3.403	002	90
14.15	3.15	3.163	101	100
18.29	2.455	2.464	102	70
-	-	2.268	003	-
22.01	2.055	2.063	110	60
-	-	1.974	111	-
23.78	1.91	1.915	103	90
-	-	1.786	200	-
25.95	1.76	1.764	112	50
26.52	1.725	1.728	201	45
26.98	1.698	1.701	004	55
29.17	1.58	1.582	202	30
30.12	1.535	1.536	104	30
-	-	1.526	113	-
33.27	1.404	1.403	203	50
-	-	1.361	005	-
-	-	1.350	120	-
35.51	1.326	1.324	121	45
35.95	1.312	1.312	114	55
37.30	1.271	1.272	105	60
37.82	1.256	1.255	212	25
-	-	1.232	204	-
40.10	1.196	1.191	300	20
-	-	1.173	301	-
41.52	1.162	1.160	213	40
-	-	1.136	115	-
42.73	1.135	1.134	006	20
43.06	1.128	1.124	302	15
-	-	1.083	205	-
45.44	1.081	1.081	106	60
-	-	1.058	214	-
-	-	1.054	303	-
-	-	1.031	222	-
-	-	1.020	221	-

Table 10. X-ray powder diffraction data for $ScI_{2.15}$

Lattice constants: $a_o = 4.08$ Å; $c_o = 6.97$ Å

θ (for Cu Kα)	d (obs) Å	d (calc) Å	hkl	Intensity	
6.40	6.9	6.97	001	15	
		3.533	100		
12.68	3.51			50)	or 95
12.77	3.485	3.485	002	50)	
14.15	3.15	3.152	101	100	
18.06	2.48	2.481	102	65	
-	-	2.323	003	-	
22.18	2.04	2.040	110	60	
-	-	1.958	111	-	
23.37	1.942	1.941	103	60	
-	-	1.767	200	-	
25.95	1.76	1.761	112	55	
26.27	1.741	1.743	004	40	
26.77	1.711	1.713	201	50	
29.20	1.579	1.576	202	35	
-	-	1.563	104	-	
-	-	1.533	113	-	
33.11	1.407	1.406	203	35	
-	-	1.394	005	-	
-	-	1.336	210	-	
35.42	1.329	1.325	114	40	
35.92	1.313	1.312	211	40	
36.30	1.300	1.297	105	30	
38.04	1.250	1.247	212	35	
-	-	1.241	204	-	
40.75	1.180	1.178	300	20	
-	-	1.162	006	-	
41.60	1.16	1.161	301	25	
-	-	1.158	213	-	
-	-	1.151	115	-	
43.50	1.119	1.116	302	15	
43.99	1.109	1.104	106	10	
44.50	1.099	1.094	205	10	
-	-	1.060	214	-	
-	-	1.051	303	-	
-	-	1.020	220	-	
-	-	1.010	116	-	
-	-	1.009	221	-	

Table 11. X-ray powder diffraction data for $ScBr_3$

Lattice constants: a_o = 3.827 Å; c_o = 6.24 Å

θ (for Cu Kα)	d (obs) Å	d (calc) Å	hkl	Intensity
7.01	6.3	6.24	001	40
13.45	3.31	3.314	100	15
14.29	3.12	3.120	002	80
15.27	2.925	2.927	101	100
19.83	2.27	2.272	102	80
	-	2.080	003	-
23.72	1.915	1.914	110	50
	1.83	1.829	111	10
25.95	1.76	1.762	103	75
	1.655	1.657	200	5
28.20	1.63	1.631	112	40
28.78	1.60	1.602	201	40
29.58	1.56	1.560	004	55
31.72	1.465	1.464	202	30
33.11	1.41	1.412	104	20
	-	1.408	113	-
36.46	1.296	1.296	203	40
38.04	1.25	1.253	210	10
	-	1.248	005	-
38.77	1.23	1.228	121	35
39.54	1.21	1.209	114	40
41.17	1.17	1.168	105	40
	-	1.163	212	-
	-	1.136	204	-
44.19	1.105	1.105	300	5
	-	1.088	301	-
45.82	1.074	1.073	213	10
	-	1.045	115	
	-	1.041	302	
47.80	1.04	1.040	006	5

Table 12. X-ray powder diffraction data for $ScCl_{1.5}$ and $ScBr_{1.5}$[a]

$ScCl_{1.5}$		$ScBr_{1.5}$	
d (Å)	Intensity	d (Å)	Intensity
8.9-9.1[b]	30	8.0-8.4[b]	60
7.7-7.8[b]	100	4.75	25
6.5	10	4.58	20
5.7	10	4.17	20
4.7	5	4.02	90
4.35-4.45[b]	10	3.49	10
3.80	15	3.18-3.20[b]	40
3.53	15	3.08	60
3.16	10	3.00	60
3.00	60	2.82-2.89[b]	80
2.87	60	2.74	60
2.72-2.78[b]	70	2.67-2.69[b]	15
2.63	45	2.56	100
2.54	35	2.475	20
2.47	70	2.31	20
2.40	5	2.225	20
2.325	15	2.16	25
2.30	10	2.095	25
2.21	45	1.99-2.01[b]	40
2.175	5	1.92-1.96[b]	20
2.12	10	1.89	35
2.06	5	1.85	10
2.00	45	1.81	60
1.85	50		
1.80	50		
1.76	50		

[a] Each pattern had many very weak lines below 1.80 Å.

[b] A range is indicated because the lines were diffuse.