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DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA

Rare Earth Metal–Metal Halide Systems. VII. The Phases Gadolinium 1.6-Chloride and Gadolinium Diiodide[1]

BY JACK E. MEE AND JOHN D. CORBETT

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The salt-rich portions of the equilibrium phase diagrams for the systems $GdCl_3$–Gd and GdI_3–Gd have been determined. The reaction of Gd with molten $GdCl_3$ is small above 632° (2 mole % Gd at 670°), but at lower temperatures the highly reduced solid $GdCl_{1.58\pm0.06}$ is formed. The probable composition limits were inferred from powder pattern data for samples with $Cl/Gd \geq 1.61$. The new compound has a salt-like electrical resistance and exhibits a paramagnetic moment of 8.0 B.M., with antiferromagnetic ordering below 50°K. The possible constitution of the phase is considered in terms of $[Xe]4f^7$-$5d^1$ and $[Xe]4f^75d^2$ states for the reduced gadolinium. A more substantial reaction of metal is found with liquid GdI_3, 14 mole % at 850°, and the phase $GdI_{2.04\pm0.04}$ separates incongruently at 831°. A practical synthesis of the pure compound was prevented by the proximity of the 825° eutectic, so that the probable composition was again bracketed from X-ray powder data for samples with $I/Gd \geq 2.11$. The brass-colored diiodide is evidently metallic in character $[Gd^{3+}(I^-)_2e^-]$ and is ferromagnetic below about 330°K. Energy and structural considerations that appear important in determining a metallic *vs.* a salt-like constitution for such compounds are also presented.

Introduction

The phenomenon of the apparent solution of metals in their molten, normal-valent halides is known for a wide variety of systems.[2] Experimental investigation of the properties of these solutions continues to support the generality first applied to post-transitional examples[3] that the process in many cases takes place with the formation of a slightly-stable, lower oxidation state of the particular element. Nonetheless, it is clear that such a broad and simple diagnosis is not immediately applicable to all situations, *e.g.*, the alkali metal solutions, and that it by no means describes the nature of the reduced solute or of the system in any detail.

If lower oxidation states are to be found in such solutions, a series of related elements with a sufficient variation in their reducibility would be expected to show a more or less gradual transition from only solution reactions to systems from which reduced solid phases also separate. Such appears to be the case in certain groups of the post-transition metals.[3] A more extensive series of this sort, with a probably more gradual change in reduction characteristics, should be found with the rare earth elements, and this appears to be true for at least the lighter members lanthanum through europium. For these, the limiting solubility of metal[4] in its molten chloride (mole %), together with the composition of the lowest of any new solid phase which results at slightly lower temperatures, are as follows.

La[5]	Ce[6,7]	Pr[9]	Nd[10]	Pm	Sm	Eu
9	9.0	18.5	30.5	...	(33)	(33.3)
...	...[8]	$PrCl_{2.31}$	$NdCl_2$	($PmCl_2$)	$SmCl_2$[11]	$EuCl_2$[11]

Substitution[9,10] and magnetic[11,12] properties of the reduced solids as well as the cryoscopic behavior of the dilute melts[9,13] all support the general formation of the corresponding M^{2+} ions throughout this series, with an increase in their stability from lanthanum through europium.

Although dilute solutions of the first four metals in their respective triiodides all exhibit comparable cryoscopic effects,[14] different and unexpected solid phases are found with higher concentrations of lanthanum, cerium, and praseodymium, *viz.*, the metallic diiodides $M^{3+}(I^-)_2e^-$.[15] Typical diiodide *salts* are then formed by neodymium and, of course, samarium and europium.[10–12] The present paper reports extension of these studies to gadolinium, where a sharp decrease in the reducibility of the tripositive ($4f^7$) ion would probably be anticipated. In fact, this is found to be true only in the molten chloride; phases with $X/Gd << 3$ occur in both the chloride and iodide systems although these are evidently very different in their properties.

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[1] Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 30 to Sept. 4, 1964. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] Reviewed by J. D. Corbett in "Fused Salts," B. R. Sundheim, Ed., McGraw-Hill Book Co., New York, N. Y., 1964, Chapter 6.

[3] J. D. Corbett, S. von Winbush, and F. C. Albers, *J. Am. Chem. Soc.*, **79**, 3020 (1957).

[4] The composition given is that at the phase eutectic or, with a lower phase, just above the melting point of the latter. The temperature coefficient of solubility in the melt in either case is positive and relatively small. Quantities in parentheses are estimated.

[5] F. J. Keneshea and D. Cubicciotti, *J. Chem. Eng. Data*, **6**, 507 (1961).

[6] G. W. Mellors and S. Senderoff, *J. Phys. Chem.*, **63**, 1110 (1959).

[7] H. R. Bronstein, A. S. Dworkin, and M. A. Bredig, *ibid.*, **66**, 44 (1962).

[8] The formation of $CeCl_2$ by a reversible reduction of solid $CeCl_3$ with H_2 was reported by S. A. Shchukarev and G. I. Novikov, *Zh. Neorgan. Khim.*, **1**, 362 (1956) (AEC-tr-5477). It is probable that the product is instead $CeHCl_2$ [compare CaHCl, P. Ehrlich, B. Alt, and L. Gentsch, *Z. anorg. allgem. Chem.*, **283**, 58 (1956)] in view of (1) the equilibrium phase results,[6] (2) the inferior reducing strength of H_2 *vs.* the metal (~60 kcal. in $\Delta H°$ for the production of $NdCl_2$), and (3) the stability of cerium hydride, which would make $CeCl_2$ even less stable toward disproportionation in the presence of H_2.

[9] L. F. Druding, J. D. Corbett, and B. N. Ramsey, *Inorg. Chem.*, **2**, 869 (1963).

[10] L. F. Druding and J. D. Corbett, *J. Am. Chem. Soc.*, **83**, 2462 (1961).

[11] Information on the better known Sm(II) and Eu(II) states is summarized by L. B. Asprey and B. B. Cunningham, *Progr. Inorg. Chem.*, **2**, 267 (1960).

[12] R. A. Sallach and J. D. Corbett, *Inorg. Chem.*, **3**, 993 (1964).

[13] A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, *Discussions Faraday Soc.*, **32**, 188 (1961).

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

[15] J. D. Corbett, L. F. Druding, W. J. Burkhard, and C. B. Lindahl, *Discussions Faraday Soc.*, **32**, 79 (1961).

Experimental

Materials.—The pure metal was obtained in the form of turnings or buttons through the courtesy of F. H. Spedding and A. H. Daane of this laboratory. Typical impurity levels were (p.p.m.) O, 300; C, 130; N, 200; F, 200; and <0.1% metallic, principally Ca, Mg, Ta, and other rare earth metals. The metal was stored in evacuated containers and used for preparations with only minimum exposure to the atmosphere. The trihalides were prepared as before[10] by allowing the metal to react directly with HCl or I_2. Even though the resulting $GdCl_3$ and GdI_3 were of good purity analytically, it was advantageous to vacuum sublime them in tantalum at least once as this not only improved their appearance (white with a slight yellow-green tint and very light gray with a green tinge, respectively) but also raised their melting points by 2 and 6°, respectively. All subsequent transfers of salt and metal were performed in a glove box under dry argon. Typical major component analysis[10] on the sublimed salts gave X/Gd ratios of 3.00 ± 0.01 with 100.00 ± 0.15% material balance. Typical impurity analyses were 500 p.p.m. O by inert gas fusion and trace quantities of Al, Si, Ca, and Mg, with Ta, W, Mo, and other rare earth elements undetected spectroscopically. Analytical results for mixtures were considered reliable if the material balance totaled 100.0 ± 0.3% or better. Values of mole % metal and X/Gd are ±0.3% and ±0.01, respectively, unless noted otherwise.

Phase Analysis.—Heating and cooling curves were obtained using essentially the apparatus and methods described earlier,[10] but with the addition of a differential thermal recording relative to a sample of Al_2O_3 which was sealed in fused silica and positioned just below the sample. Tantalum radiation shields just above the sample, shielded thermocouple leads, and a grounded Inconel furnace liner were found to improve the quality of particularly power-on data at the higher temperatures. Thermocouples were checked against the melting points of Ag, NaCl, and NaI. Thermal halts were reproducible to ±1° on a given sample and, unless otherwise noted, all fixed temperatures are thought to be ±1°. The only notable supercooling was observed with $GdCl_3$, up to 16°.

The compositions of the salt-rich liquids in equilibrium with metal were determined by rapid quenching of the sample from temperature followed by analysis of the salt matrix. For this a sealed length of 0.25-in. tantalum tubing containing salt and metal buttons or chunks was suspended from a tantalum wire axially in a heated section of fused silica tubing to which Pyrex end pieces were attached *via* $\mathrm{\overline{\$}}$ joints. The latter were cooled with small blowers during operation. The upper part contained a connection for evacuation during the equilibration, two lead-throughs for the thermocouple, the junction of which was in contact with the tantalum tube, and a hook attached to the outer piece of a horizontal $\mathrm{\overline{\$}}$ joint so that rotation of the latter dropped the sample. The lower piece contained silicon quenching oil and a submerged wad of glass wool to break the fall of the sample.

The best method for isolation of the lower gadolinium chloride was by equilibration with excess metal in a temperature gradient. In one method, sufficient salt and metal were loaded into a 5-in. length of 0.25-in. tantalum tubing to fill the tube to *ca.* 3 in. after the salt had been melted, and this was placed in a $^5/_{32}$-in. i.d. evacuable silica container equipped as above so that a thermocouple was in direct contact with the sample tube. Two small $^3/_8$-in. i.d. furnaces were positioned above this and adjusted so that most of the sample was at 650° but the top part was at 600°, and the sample was then slowly raised over a period of several days. In another variation, the sample was slowly lowered in a Marshall furnace which had been adapted so that the container was in a uniform temperature gradient of *ca.* 14° in.$^{-1}$. The product yield by either method was low but the crystals were large enough so that they could be separated from the bulk salt by hand sorting in a drybox.

Powder Pattern Data.—The X-ray diffraction data for powdered samples were collected as before.[10] The stronger lines for $GdCl_{1.6}$ in Å., with relative intensities in parentheses, are: 8.97(3), 7.22(6), 4.95(2), 3.38(4), 3.04(2), 2.464(10), 2.358(6), 2.251(2), 1.983(3), 1.799(3). The complete set can be indexed on the basis of an orthorhombic unit cell 8.98 × 7.22 × 6.72 Å. For GdI_2, the data are 7.43(3), 2.88(7), 2.50(8), 2.285(3), 2.033(3), 1.878(10), 1.659(3), 1.380(6), 1.274(5); a hexagonal cell with a_0 = 8.67, c_0 = 5.75 Å. accounts for all of the data. A prototype structure for either phase was not found.

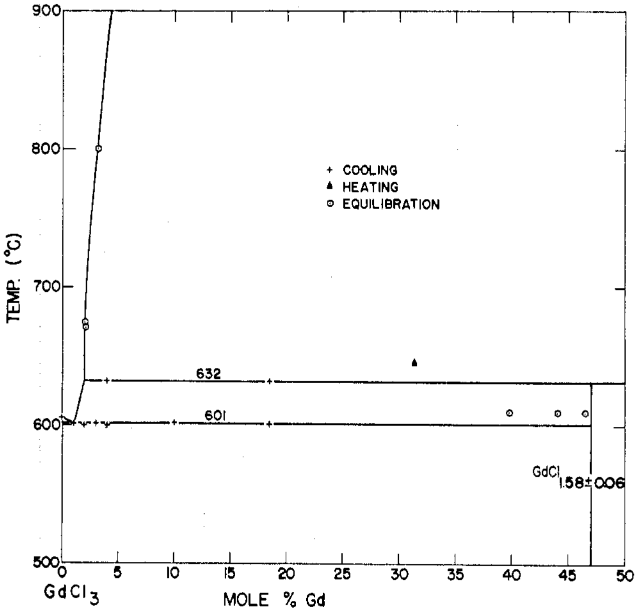

Figure 1.—The salt-rich half of the equilibrium phase diagram for the $GdCl_3$–Gd system. Metal is in equilibrium with the $GdCl_3$-rich solution above 632° and with $GdCl_{1.58}$ at lower temperatures.

Results

Gadolinium(III) Chloride–Gadolinium.—The relatively simple equilibrium phase relationships are illustrated in Figure 1. The 605° melting point of $GdCl_3$ (lit.[16] 602°) is depressed to a eutectic at 601° by 1.0 ± 0.5 mole % Gd, and at higher temperatures the limiting solubility increases only slowly, 2.0% at 670°, 3.2% at 800°, and 5.0% at 950°. The magnitude of the interaction (above 632°) is the smallest known for any rare earth metal trihalide system.

Certainly the most remarkable feature of the system is the indicated existence of a solid compound near $GdCl_{1.6}$ in composition, a fact that probably would have been missed without thermal analysis studies. Preparation of well-reduced samples and deduction of the composition of the lower phase was accomplished with some difficulty. At first, efforts were made to obtain the product by the direct reaction of $GdCl_3$ and excess Gd for 10 to 20 days between the indicated eutectic and peritectic temperatures, 601 and 632°, respectively. However, such products subsequently analyzed near 33 mole % metal (*i.e.*, Cl/Gd $\sim$ 2.0) and they still exhibited a large eutectic halt on cooling. In addition, their powder patterns showed the presence of appreciable amounts of $GdCl_3$; in fact, only the characteristic trichloride lines were evident at the composition $GdCl_{2.46}$ and these were still of major intensity at $GdCl_{2.11}$. The best yields of the reduced phase were eventually ob-

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(16) F. H. Spedding and A. H. Daane, *Met. Rev.*, **5**, 297 (1960).

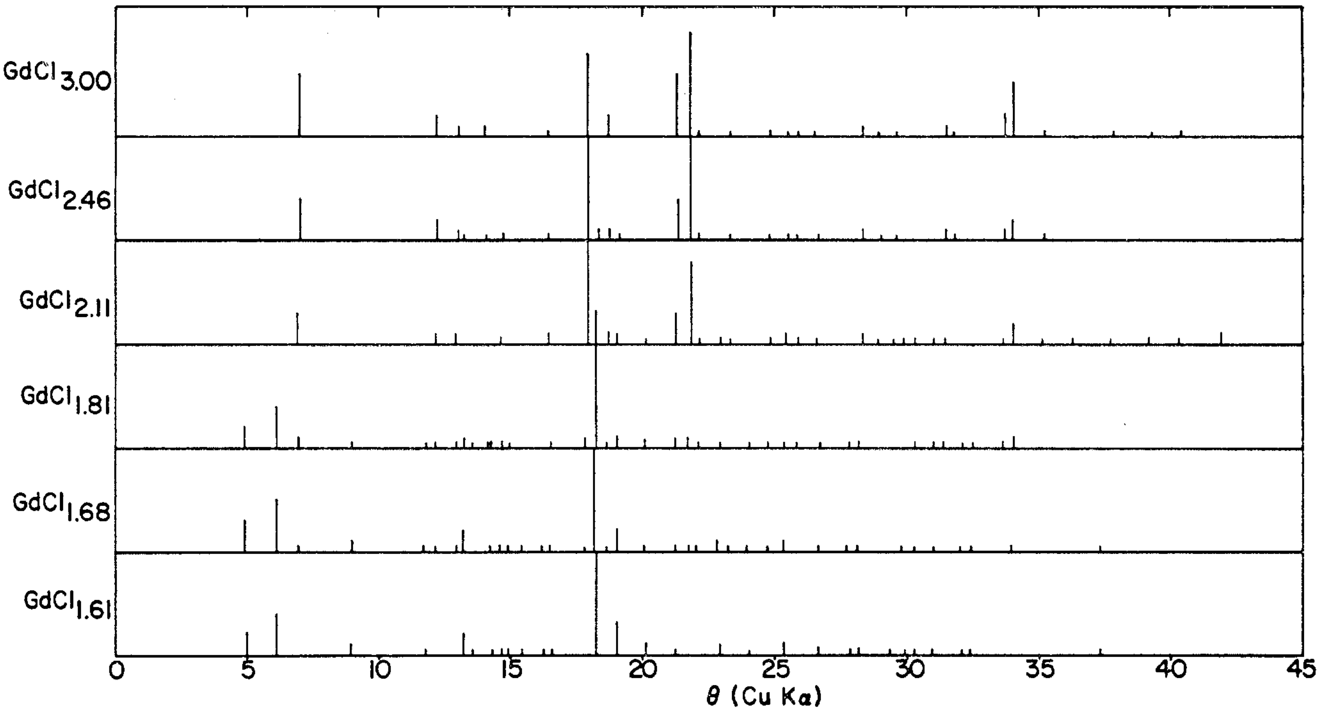

Figure 2.—X-Ray powder diffraction data for gadolinium chloride samples.

tained by equilibration under a temperature gradient (see Experimental section). Single crystals up to 0.25 in. in length could then be sorted from the bulk, although varying amounts of the salt matrix would sometimes cling to them. In this way small samples of the compositions $GdCl_{1.81\pm0.03}$, $GdCl_{1.68\pm0.03}$, and $GdCl_{1.61\pm0.03}$ were obtained.

The probable composition of the lower phase has been bracketed between about $GdCl_{1.64}$ and $GdCl_{1.52}$ by the following reasoning. As illustrated in Figure 2, the presence of $GdCl_3$ is evident in the powder patterns down to $GdCl_{1.68}$, and only the lowest sample obtained, $GdCl_{1.61}$, is free of the higher phase within the sensitivity of this method. With regard to the stronger lines from each phase it appears that the diffracting power of the *hkl* planes responsible in $GdCl_3$ is at least twice that in $GdCl_{\sim 1.6}$, since the two phases have their stronger lines equal in intensity at about the composition $GdCl_{2.0}$. The lower limit of $GdCl_{1.52}$ given then results from the pessimistic assumption that a maximum of 6% $GdCl_3$ (that is, 12% of a phase of equal diffracting power) could have gone undetected at $GdCl_{1.61}$. Correspondingly, the upper limit of $GdCl_{1.64}$ is obtained from the contrary, optimistic presumption that as little as 3% $GdCl_3$ could have been responsible for its observation at $GdCl_{1.68}$. The result is thus $GdCl_{1.58\pm0.06}$, neglecting any errors in analysis; hereafter the phase will be referred to as $GdCl_{1.6}$.

Single crystals of the phase occur as dark gray to black needles with a dark brass to brown reflectance. At least some of these turn out to be bundles of fibrous crystals of very small cross section. All showed lengthwise resistances of *ca.* 10^7 ohms over $^1/_8$ to $^1/_4$ in. when measured with a VTVM in a drybox, so that the compound is evidently salt-like as opposed to metallic.

The magnetic susceptibilities of 38- and 76-mg. samples with a Cl/Gd ratio of 1.7 to 1.8 were measured by the Faraday method. The results[17] below 289°K. were corrected for traces of the ferromagnetic Gd impurity (~10 and 300 p.p.m. in the two cases) by extrapolation to infinite field of (Honda–Owen) plots of χ_T(obsd.) *vs.* H^{-1}. The resulting $\chi_{T,\infty}$ data for temperatures between 80 and 360°K. are described very well by the Curie–Weiss relationship, with a slope that corresponds to a moment of 8.00 ± 0.05 B.M. and a Weiss constant Δ of about 165° (without correction for the small $GdCl_3$ content). The latter forecast of incipient ordering was borne out by measurements made with a mutual inductance bridge,[18] which revealed a clear antiferromagnetic transition at 50°K.

Gadolinium(III) Iodide–Gadolinium.–The most noteworthy aspect of this system (Figure 3) is the existence of a stable solid with an apparent stoichiometry near GdI_2. Efforts to obtain the pure phase were somewhat frustrated by the small separation between the 831° melting point and the 825° eutectic. Even with care, samples equilibrated between these points usually cycled over the peritectic temperature so that any diiodide already formed disproportionated into finely-divided metal and melt, making the bulk composition variable and meaningless. A sample of composition $GdCl_{2.11}$ was finally obtained by equilibration of triiodide with excess metal for 10 days at 5 to 10° below the apparent eutectic temperature. On cooling, the eutectic transition was (for unknown reasons) then observed as low as 808°, and, with continued reaction, this effect gradually grew smaller and finally practically

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(17) J. D. Greiner, *et al.*, to be published.

(18) B. C. Gerstein, Ph.D. Thesis, Iowa State University, Ames, Iowa 1960.

disappeared while the diiodide transition at 670° became progressively more pronounced. Isolation of the high temperature form of GdI_2 by quenching was not successful.

The probable composition $GdI_{2.04\pm0.04}$ for the lower phase was again estimated on the basis of powder pattern data. Diffraction due to the diiodide was first observed at the composition $GdI_{2.64}$ and was equal to that for GdI_3 near $GdI_{2.35}$. Since GdI_3 was almost absent at $GdI_{2.11}$ the lower phase would be at $GdI_{2.08}$ if as little as 3% GdI_3 could have been detected. This may be a little high since extrapolation of the intensities for the minor component indicated that the triiodide would not have been detected at about $GdI_{2.06}$. In the latter case an upper limit of 6% GdI_3 places the phase at $GdI_{2.00}$. Some support for the lower composition is also given by the observation that the thermal effect of the eutectic first appears at $GdI_{2.92}$, or 19% of the eutectic composition, and it is practically gone at $GdI_{2.11}$, where an equal amount of eutectic would place the phase at $GdI_{2.01}$.

The 931° melting point observed for GdI_3 compares to a recent literature value of 925°.[16] The additional thermal effect at 740° is evidently due to a previously unreported phase transition; the high temperature phase could not be isolated by quenching from above 740°.

There is one portion of the diagram (Figure 3) that remains unexplained, the thermal effect or effects shown in the 840–850° region for GdI_3-rich compositions. With a given sample at least one and frequently two inflections in both the temperature and the differential recordings were observed in this region, with magnitudes about the same as for the liquidus. If the effect were due to the formation of an incongruently melting, intermediate compound, then the eutectic transition would not be observed on cooling a sample richer in iodide after adequate equilibration between the eutectic and possible peritectic temperature. Similarly, compositions richer in metal than such a phase should not exhibit the triiodide transformation at 740° after a similar equilibration. Furthermore, either a new phase should be evident in X-ray data or its disproportionation at lower temperatures should be found. In fact, the thermal effect of neither the eutectic nor the GdI_3 phase transition was significantly reduced by equilibration at 830° for 3 days, and no evidence could be found either for a new phase in room temperature X-ray data or for an obvious decomposition below 825°. The possibility that the enigmatic thermal effect(s) was due to an induced transformation in GdI_3 was also eliminated when nothing was observed in this region with samples containing 1 and 2 mole % Gd. The only explanation which appears to remain is that the 850° effect is due to the peritectic formation of a new phase ($2.7 < I/Gd < 2.9$) which in turn disproportionates at about 840°.

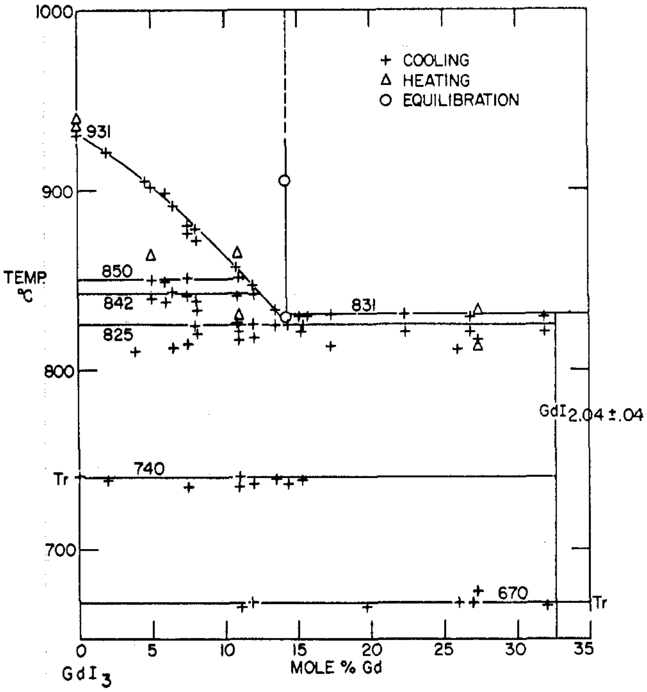

Figure 3.—The salt-rich portion of the equilibrium phase diagram for the system GdI_3–Gd. The 831 and 670° horizontals extend to the right to pure metal.

Gadolinium diiodide is a bright, brass-colored solid that is strongly attracted to a magnet. Preliminary Faraday measurements of the magnetic susceptibilities of the $GdI_{2.11}$ composition between 300 and 77°K. show that the material is clearly ferromagnetic, saturating at *ca.* 2 koersteds over this range with $T_C \sim$ 320–340°K. The saturation magnetization at 8 koersteds and 0°K. obtained from a linear $T^{3/2}$ plot is only about 20% of that expected for spin-parallel ferromagnetism of a $^8S_{7/2}$ state, suggesting the presence of less complete alignment (*e.g.*, helical or ferri-) in GdI_2.

Qualitative resistance measurements on the lower iodide indicate it is probably metallic in character and should therefore be formulated as $Gd^{3+}(I^-)_2e^-$. Actually, the lowest composition obtained, $GdI_{2.11}$, exhibited a resistance of about 10 kilohms between all points contacted on a piece about 0.75 × 1 in. in size. However, the sample was finely polycrystalline and homogeneous in appearance, and the uniform distribution of about 11% of the insulating GdI_3 is thought to be responsible for the high value. In contrast, a number of samples in the range of $GdI_{2.8}$ to $GdI_{2.3}$ had typical resistances as low as 30 ohms between some points and as high as 10^5 between others. In these cases the samples, although richer in GdI_3, were also highly segregated with brassy GdI_2 crystals scattered throughout the gray matrix. Since appreciable contact resistance may be present as well, as with LaI_2 and CeI_2,[19] it is concluded that the lower phase is probably metallic, although the evidence is not as conclusive as it might be, largely because of the extreme difficulty experienced in obtaining a relatively pure sample.

Discussion

As anticipated in the Introduction, products of the reduction of liquid $GdCl_3$ apparently have a low stability in the melt since the solubility of metal therein is

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(19) R. A. Sallach and J. D. Corbett, to be published.

generally small (Figure 1). On the other hand, the additional formation of the unusual solid $GdCl_{1.6}$ could scarcely have been anticipated. It is evident that the new compound is only slightly stable with respect to disproportionation; $\Delta F°_{902}$ for the formation of $GdCl_{1.6}$ from Gd(s) and $GdCl_3$(l) is only about 30 to 60 cal./g.f.w., the indicated range arising from the choice of solute, and hence the mole fraction of $GdCl_3$, in the presumed ideal solution in equilibrium.

With regard to the constitution of this compound, it seems proper to consider it as salt-like and hence a truly reduced gadolinium in view of its high electrical resistance. The presence of more than one formal oxidation state in some particularly stable lattice seems evident, and two limiting cases can be considered on the basis of the stoichiometry, approximately $(0.6\ Gd^{II}, 0.4\ Gd^{I})Cl_{1.6}$ (A) and $(0.3\ Gd^{III}, 0.7\ Gd^{I})Cl_{1.6}$ (B). The magnetic susceptibility results do not enable these to be distinguished although they do put some limits on the electronic configurations possible. Since the observed paramagnetic moment, 8.0 B.M., is the same as theory for Gd^{3+} (7.94 B.M.) to well within the usual variations observed experimentally, this then clearly eliminates from further consideration the possible configurations $[Xe]4f^8$ $(^7H_6)$ and $[Xe]4f^9$ $(^6H_{15/2})$ for the reduced gadolinium, as these have moments near 9.7 and 10.6 B.M., respectively.[20]

Arrangements which could account for the magnetic "disappearance" of the extra 1.4 electrons apparently all require that these be in the more available and reactive 5d state (or higher). Obviously, spin pairing through the formation of metal-to-metal bonds between all reduced ions would leave only the $4f^7$ core observable. Pairing of the outer electrons in Gd^+, $4f^75d^2$, as a result of a large "crystal field" or spin–orbit coupling would do likewise. Only two other situations have been found that have the observed moment and satisfy the approximate stoichiometric formulations A or B above if states involving noninteracting 6s or 6p electrons (*e.g.*, $4f^76s^2$) are ruled out. These are, both with case A, the fortuitous combinations of $4f^75d^1$ and $4f^75d^2$ for Gd^{2+} and Gd^+, with one *or* the other exhibiting a spin-only contribution from the 5d electrons to give average moments of 7.84 or 7.89 B.M., respectively. Rather than speculating further how these might come about, it seems pertinent to observe that all possibilities probably differ from those for diamagnetic compounds of the heavy transition metals in formal d^1 and/or d^2 states only by the addition of the "inert" $4f^7$ electrons. The apparent conclusion that reduction of gadolinium(III) leads to ions with an effective ground state of $[Xe]4f^75d^2$, and possibly $[Xe]4f^75d^1$ as well, is not without precedent, however, since the latter is known for Gd^{2+} in cubic sites in host lattices.[21] It is clear that further clarification of the constitution of $GdCl_{1.6}$ as well as a meaningful interpretation of its antiferromagnetism at lower temperatures probably must await the determination of its crystal structure.[22]

The present findings also bring to mind the time-honored status of the $4f^7$ configuration in the chemistry of the rare earth elements and the special stability thus accorded to gadolinium(III). Although in the past this has even been taken to mean a complete inertness of this state, more cautious statements have pertained only to its resistance to oxidation.[23] On the other hand, "inertness" of the $4f^7$ electrons to reduction is not violated in the usual sense if such reactions lead to $4f^75d^n$ states, as appears to be the case. It is also clear that electronic structure even in the 4f shell can no longer be considered the sole factor in determining the existence of reduced (or oxidized) ions. Although such a special configuration is encountered with Eu^{2+} (and Yb^{2+}), and the more questionable tendency to "approach" this cited as important in the existence of Sm^{2+} (and Tm^{2+}), the formation of Nd^{2+} $(4f^4)$[10,12] and evidence for even Pr^{2+}[9] and Ce^{2+}[10] in the solid state certainly must mean that other thermodynamic factors are also very important.

Substitution of iodide for chloride in rare earth metal systems sometimes leads to large, irregular, and apparently specific differences rather than just a small increase in the limiting reduction of the melt and in the stability of a lower oxidation state. The contrast between the limited reduction of the chloride (and bromide) melts of lanthanum through praseodymium (see Introduction) and the large solubility of the corresponding metals in their iodides with the formation of metallic diiodides at lower temperatures is particularly striking. Gadolinium would also appear to be in this class, judging from the marked increase in solubility of metal (from 3.5 to 14.2% at 850°) and the apparent formation of a metallic diiodide. Although the freezing point depressions for dilute solutions of the light metals in their iodides are still consistent with a M^{2+} solute, cryoscopic numbers for dilute solutions of Gd in GdI_3 can only be roughly estimated (at 2.0 to 2.8 compared to 3.0 for Gd^{2+}, 1.5 for Gd^+) because of the lack of a reliable heat of fusion. Intrusion of the phase transformation at 740° also makes its estimation from known data for the lighter triiodides rather uncertain. The transition in GdI_3 appears to be depressed by about 2° on addition of metal, suggesting solid solutions as an additional complication.

At present, further understanding of the rare earth metal–metal iodide solutions largely results from their conduction properties[14] and from the nature of the diiodide phases that separate at lower temperatures. Certainly there are not sufficient data available to predict the relative stabilities of any series of reduced, ionic salts, such as from a Born–Haber cycle. However, it does appear possible to make some pertinent

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(20) D. M. Yost, H. Russell, Jr., and C. B. Garner, "The Rare Earth Elements and Their Compounds," John Wiley and Sons, New York, N. Y., 1947, p. 14.

(21) D. S. McClure and Z. Kiss, *J. Chem. Phys.*, **39**, 3251 (1963).

(22) If the apparent unit cell volume (see Experimental section) is correct, reasonable radii of the possible ions and the presumption that 65 to 85% of the free volume will be occupied allow only Gd_7Cl_{11}, with an atom ratio of 1.57, in the stated range of 1.58 ± 0.06. Other possibilities, Gd_6Cl_{10} (1.67) and Gd_8Cl_{12} (1.50), lie slightly outside of the probable limits. All are compatible with either the A or B formulation.

(23) Reference 20, p. 6.

and useful observations regarding factors which appear important in determining whether a salt-like $[M^{2+}(I^-)_2]$ or a "metallic" $[M^{3+}(I^-)_2e^-]$ diiodide is to be formed if such a composition occurs at all. In this case the enthalpy change for the transformation

$$M^{2+}(I^-)_2\,(s_1) = M^{3+}(I^-)_2e^-\,(s_2)$$

is $-U_1 + I_3 + U_2$. The metallic state presumably has the larger lattice energy because of the enhanced interactions of the higher-charged cation with both the anions and the delocalized electrons. To a first approximation it might be supposed that the rare earth metal diiodides should show relatively constant values for $U_2 - U_1$, or differences which change relatively smoothly. The fact that the change is resisted by I_3 brings to mind two general guidelines which may be useful in assessing where and under what conditions such metal-like iodides may be encountered. First, it is evident that such will be favored by low values of I_3, and certainly the rare earth elements and a few neighbors in the periodic table are the most likely candidates to meet this requirement. Similarly, the apparently metallic $Th^{4+}(I^-)_2(e^-)_2$[24] results for that tetrapositive element which probably has the smallest value for $(I_3 + I_4)$, although we are obviously not prepared to explain why a metallic thorium triiodide did not form also or instead. Extension of this idea to normally dipositive metals would suggest that barium would present the most likely (practical) candidate for a $M^{2+}I^-e^-$ phase; however a recent, critical examination of the BaI_2–Ba system indicates that no such intermediate (or any other) is formed.[25]

A second important condition, one which may actually supplant the first for heavy elements, can be placed on the electronic state of the reduced metal ion if a metal-like example is to occur. Obviously 4f orbitals, highly shielded and with small radial extension, are not likely candidates for the formation of the necessary conduction band. Hence the divalent ion derived from a M^{3+} ion with a $4f^n$ configuration should probably be $[Xe]4f^n5d^1$, or not far removed from this, in order for the extra electron to be delocalized into a conduction band that probably has a substantial amount of 5d character.[2,19,26] This appears to be the case for La, Ce, Gd (and Th).[21] In this light NdI_2 and the diiodides of Sm, Eu, Tm, and Yb are salt-like simply because the added electron is well buried in the 4f shell. The same consideration may also be pertinent with the salt-like UI_3[27] and in the conduction properties of MX_3–M melts.[14,19] The role of the iodide ion is less clear, although it is obviously important since "metallic" phases have not been found with either chloride or bromide.

Finally, the ferromagnetism observed for GdI_2 is not particularly surprising since conduction electrons would provide a ready mechanism for coupling of $4f^7$ cores, as in the metal. Magnetic orientation may also be present in CeI_2 and PrI_2.

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CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC CHEMISTRY,
BRISTOL UNIVERSITY, BRISTOL, ENGLAND

Chemistry of the Metal Carbonyls. XXVIII. Addition of Rhenium Pentacarbonyl Hydride to Fluoroolefins[1,2]

BY J. B. WILFORD[3] AND F. G. A. STONE

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This paper describes the addition of rhenium pentacarbonyl hydride to the compounds $CF_2{=}CF_2$, $CF_2{=}CFCl$, $CF_2{=}CCl_2$, and $CF_3C{\equiv}CCF_3$, and the nature of the rhenium complexes obtained. The reaction between tetrafluoroethylene and methylrhenium pentacarbonyl is described and compared with that involving methylmanganese pentacarbonyl.

In previous papers we have described several fluorocarbon–transition metal complexes prepared by addition of the hydrides $HMn(CO)_5$, π-$C_5H_5Mo(CO)_3H$, or π-$C_5H_5W(CO)_3H$ to tetrafluoroethylene, by addition of $HMn(CO)_5$ to chlorotrifluoroethylene, 1,1-dichloro-2,2-difluoroethylene, or hexafluorobut-2-yne, and by addition of methylmanganese pentacarbonyl to tetrafluoroethylene or chlorotrifluoroethylene.[4] Continuing these studies we have investigated reactions between rhenium pentacarbonyl hydride and these unsaturated fluorocarbons. The addition of methylrhenium pentacarbonyl to tetrafluoroethylene is also described. The na-

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(3) Department of Scientific and Industrial Research predoctoral student.

(4) (a) For a summary of this work see P. M. Treichel and F. G. A. Stone, *Advan. Organometallic Chem.*, **1**, 143 (1964); (b) J. B. Wilford, P. M. Treichel, and F. G. A. Stone, *J. Organometallic Chem.*, **2**, 119 (1964).