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# Magnetic Susceptibilities of Neodymium(II) Chloride and Iodide[1]

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The magnetic susceptibilities of $NdCl_2$ and $NdI_{1.95}$ over the range 77 to 550°K. as well as those of $NdCl_3$ and $NdI_3$ between 77 and 480°K. have been determined by a standard Gouy technique. The trichloride and triiodide obey the Curie–Weiss relationship and yield 3.78 B.M. ($\Delta = 31°$) and 3.72 B.M. ($\Delta = 9°$), respectively, for the cation moment, which compare with the theoretical value of 3.62 B.M. for the $^4I_{9/2}$ ground state of $Nd^{3+}$. Thermal population of the first excited state is important in the neodymium(II) state, as predicted by van Vleck. The data for both salts are well described with moments of 2.87 and 5.36 B.M. for the ground and excited states and $\Delta E/k = 1400°K$. The theoretical values are 2.68 and 4.93 B.M. for the $^5I_4$ and $^5I_5$ states, respectively. The results confirm the presence of the reduced $4f^4$ ion $Nd^{2+}$ in the neodymium(II) halides that is suggested by the conduction properties of the solid and liquid salts. The reported susceptibility of $Pm^{3+}$ is also considered.

The existence of several reduced halides of neodymium has been established in the course of a general study of the reactions of the rare earth metals with their respective trihalides.[2] In the Nd–$NdCl_3$ system there are three new compounds, all melting incongruently, the stoichiometric $NdCl_2$ and two intermediate phases, $NdCl_{2.37}$ and $NdCl_{2.27}$. On the other hand, the phase diagram of the Nd–$NdI_3$ system reveals only one intermediate compound, the congruently melting $NdI_{1.95}$ (hereafter termed a diiodide for convenience). While the corresponding bromide system has yet to be investigated, the probable existence of at least a dibromide can be inferred.

The known dihalides of neodymium are electrically insulating and are thus in contrast to the diiodides of lanthanum, cerium, and praseodymium in that the latter are good conductors.[3] It has been shown that at least in $LaI_2$ the rare earth element is present in the tripositive state with the third valence electron delocalized in a metallic conduction band.[4] Accordingly, the insulating character of the two neodymium dihalides strongly suggests the presence of the dipositive cation. This view is also supported by the electrical conductivity of the $NdX_3$–$NdX_2$ melts in that the conduction appears to be substantially that of a mixture of ionic substances with little electronic contribution, in contrast to the behavior of the corresponding lanthanum, cerium, and praseodymium systems.[5–7] In order to verify the existence of the $Nd^{2+}$ ion, magnetic susceptibility measurements have been carried out on the dichloride and diiodide. Data have also been secured for $NdCl_3$ and $NdI_3$.

## Experimental

**Apparatus.**—The magnetic susceptibilities were determined by the standard Gouy technique using powdered samples. A water-cooled 4-in. electromagnet was used to produce fields up to 8 kgauss. The magnetic field strength was stabilized at any given value by means of an electronic current controller[8] that reduced field fluctuations to <1 gauss. The magnitude of the magnetic field was calculated from the measured value of the proton resonance frequency in $H_2O$ as observed with a Pound magnetometer.

Standard Gouy tubes of precision bore Pyrex tubing were suspended from an analytical balance and within a long copper tube that was integral with the balance case. A slow flow of either dry $N_2$ or He gas was maintained through the tube and case except during weighings. A dewar assembly (for $T < 300°K.$) or an oil bath (for $T > 300°K.$) surrounded the copper tube. Temperature was measured by three equally spaced thermocouples mounted on the exterior of the copper tube at positions corresponding to the top, middle, and bottom of the sample. These couples were chromel–alumel for $T > 300°K.$ and calibrated copper–constantan for lower temperatures.

**Materials.**—The metal employed was obtained through the courtesy of Drs. F. H. Spedding and A. H. Daane and contained 0.08% Pr, <0.06% Sm, <0.01% Fe, 0.1% Ta, 0.03% C + N + F, and 0.06% O. The trihalides were prepared as previously described.[2,8] In addition, the trihalides used directly for susceptibility studies were vacuum sublimed in an all-tantalum apparatus. This effectively removed a dependency of $\chi$ on $H$ at <4 kgauss that was otherwise present, especially in the triiodide.

The dihalides were made by equilibration of the respective trihalide with excess metal in Ta containers under Ar. In the case of $NdCl_2$, the reactants were heated to ~860° and maintained at this temperature for 12 hr. Following this the temperature was lowered below the incongruent melting point of $NdCl_2$ (to ~825°) and equilibrated for an additional 6 hr., and the sample was then quenched. For the preparation of the diiodide, the temperature was first raised to above 800° for several hours and then lowered to ~580°, and the equilibration was continued for a total time of 12 hr. No additional equilibration of the solid phase was required since the diiodide melts congruently. These long equilibration times were necessary due to the relatively viscous nature of the melts. The use of sublimed trihalide salts in these preparations was deemed unprofitable because any impurities removed by sublimation (principally O, 600 p.p.m. in one case) would be reintroduced during the equilibration with excess metal. Chemical analyses of the dihalide products yielded X:Nd atom ratios of 2.04 ± 0.01 and 1.95 ± 0.01 for the chloride and iodide

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(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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

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

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

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

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

(7) A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, *ibid.*, **67**, 2715 (1963).

(8) W. M. Hansen, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1956.

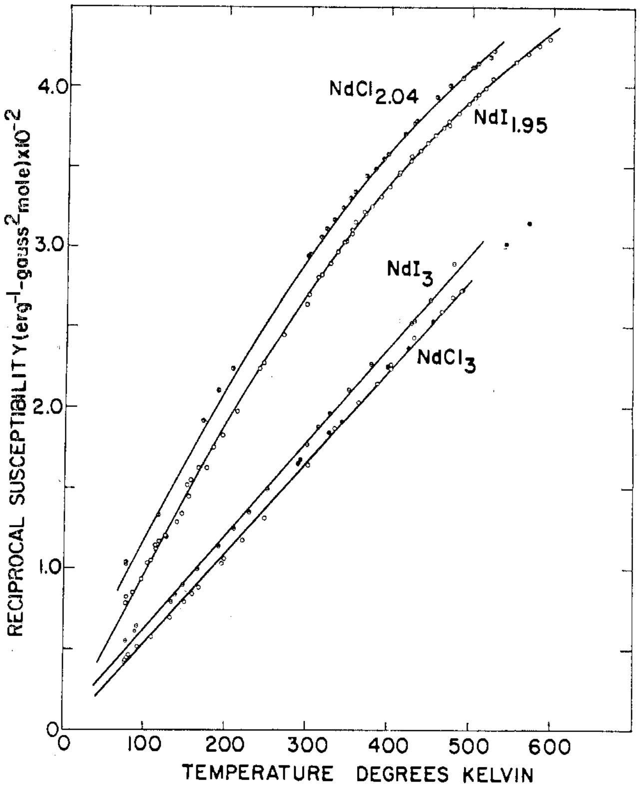

Fig. 1.—Reciprocal paramagnetic susceptibilities of the neodymium(III) and neodymium(II) chlorides and iodides. For clarity the data for $NdCl_3$ have been displaced downward by 0.2 unit in $1/\chi_M \times 10^{-2}$, and the data for $NdCl_{2.04}$ have been displaced upward by 0.2 unit. The solid circles for $NdCl_3$ are the data of Sanchez (ref. 12).

samples, respectively. The chloride was used as such although it was not completely reduced. A small increase in $\chi$ was observed only when $H$ was reduced to less than 3 kgauss.

## Results and Discussion

The results for the four compounds are illustrated in Fig. 1 as $1/\chi_M$ *vs.* $T$, where $\chi_M$ is the experimental molar susceptibility corrected for the small, underlying diamagnetism of the ions. The values given by Selwood[9] were used for the latter, *i.e.*, in $10^6$ erg gauss$^{-2}$ mole$^{-1}$, $-26$ for $Cl^-$, $-52$ for $I^-$, and $-20$ for $Nd^{3+}$. The value of $-23$ for $Sm^{2+}$ was used for $Nd^{2+}$.

As is seen, the behavior of the trihalides between 79 and 500°K. is adequately represented by a Curie–Weiss equation

$$\chi_M = C/(T + \Delta)$$

where $C$ is the Curie constant and $\Delta$ is the Weiss or "molecular field" constant.[10] The constants $C$ and $\Delta$ have the values of 1.769 and 31° for $NdCl_3$ and 1.716 and 9° for $NdI_3$. The magnetic moments calculated for $Nd^{3+}$ from the $C$ values are 3.78 B.M. in the chloride and 3.72 B.M. in the iodide. For $Nd^{3+}$ theory predicts a value of 3.62 B.M. for the temperature-dependent portion of the moment $[gJ(J + 1)]$ for the $^4I_{9/2}$ ground state.[9,11] The only previous magnetic data for the anhydrous neodymium trihalides are from the work on $NdCl_3$ by Sanchez,[12] who prepared the compound by dehydration of the hydrated salt in an atmosphere of HCl. According to his data, $C = 1.861$, $\Delta = 57°$, and $\mu = 3.87$ B.M. The solid circles shown in the figure are his data recalculated to include a diamagnetic core correction for $Nd^{3+}$. Although the range of the previous work is much shorter, the earlier data differ from those of this work substantially only at room temperature.

It can readily be seen in Fig. 1 that the Curie–Weiss relationship is not obeyed by the dihalides, although there is evidently an asymptotic approach to this at lower temperatures to give $\mu \sim 2.8$ B.M. and $\Delta \sim 0$. Such behavior can, in analogy to that of $Sm^{3+}$ and $Eu^{3+}$ ($Sm^{2+}$), be attributed to the presence of a low-lying excited level, as predicted by van Vleck many years ago.[11] From Hund's rules the ground state for the $4f^4$ configuration would have the term $^5I_4$ and the first excited state, $^5I_5$. The data can therefore be analyzed in terms of the theoretical expression[9,11] for the effective moment of a system involving thermal population of higher states with different moments. In the present case it is assumed that only the first excited state need be included and that any crystal field effects in splitting either state are negligible. If just $\Delta E$, the separation of the two states, is allowed as a parameter, only a very rough correlation with the experimental data can be obtained. However, a very satisfactory fit can be achieved if the effective magnetic moments of the two states are also used as parameters but with the ground and first excited states still taken to be nine- and elevenfold degenerate, respectively (*i.e.*, $J = 4$ and 5). Successive approximations with the more complete data for the diiodide yield $\Delta E/k = 1400$°K., $\mu$ ($^5I_4$) = 2.87 B.M., and $\mu$ ($^5I_5$) = 5.36 B.M. The theoretical values are 2.68 and 4.93 B.M., respectively. The separation of states appears reasonable judging from rough estimates that can be made using the known values for $Nd^{3+}$, $Sm^{3+}$, and $Eu^{3+}$ (summarized in ref. 13) together with approximate $Z$–$S$ functions.[11]

The solid curves for the dihalides in Fig. 1 are drawn according to the derived parameters. The data for the two salts are almost superimposable despite the difference in stoichiometry. Neither the presumed 4% $Nd^{3+}$ content of the dichloride sample used nor any possible source of the iodide deficiency in $NdI_{1.95}$ (*e.g.*, 5% $Nd^+$ ?) appears significant in the present data.

The magnetic data satisfactorily confirm the $4f^4$ configuration of the cation in the two neodymium dihalides as well as the presence of the expected, low-lying level excited state. Of prime significance is the fact that experimental studies can now be made of the $4f^4$ con-

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[9] P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956, pp. 78, 137.

[10] There is perhaps a small hint of curvature in this function at the lower temperatures. This would suggest a crystal field splitting of the ground state that is becoming comparable with $kT$.

[11] J. H. van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, England, 1932, Chapter IX.

[12] A. C. Sanchez, *Rev. acad. cienc. exact., fis., y nat. Madrid*, **34**, 202 (1940).

[13] W. T. Carnall, D. M. Gruen, and R. L. McBeth, *J. Phys. Chem.*, **66**, 2161 (1962).

figuration using convenient, though chemically reactive, materials, Heretofore, this state has been available only in the rare and radioactive promethium(III) compounds. In this connection, Sheppard, *et al.*,[14] have recently made the difficult measurement of the susceptibility of $^{147}Pm^{3+}$ in the oxide at room temperature. Their result of 2780 $\times 10^{-6}$ erg gauss$^{-2}$ mole$^{-1}$ for $\chi_M$ (298°) (corrected for core diamagnetism) compares with an average of 3720 $\times 10^{-6}$ obtained here with the isoelectronic $Nd^{2+}$ and a 2980 $\times 10^{-6}$ value calculated from the theoretical moment with the questionable assumption of $\Delta E >> kT$ (and $\Delta \sim 0$). It should be noted that population of the first excited state will *increase* $\chi_M$. In the dihalides this thermal effect is about (290 ± 60) $\times 10^{-6}$ e.s.u. in $\chi_M$ at room temperature, and it would be expected to be somewhat less for $Pm^{3+}$ on the basis of $\Delta E/k \sim 2300$°K. estimated from analogous values for the neighboring, tripositive ions.[11,13] The difference observed for $\chi_M$ for $Pm^{3+}$ may be due either to an effective moment that is lower than theory or to a significant self-heating of the sample.

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[14] J. C. Sheppard, E. J. Wheelwright, and F. P. Roberts, *J. Phys. Chem.*, **67**, 1568 (1963).

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# Protactinium Fluorides[1]

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Several protactinium fluorides have been prepared with 5 to 200 mg. amounts of $Pa^{231}$. The tetrafluoride, $PaF_4$, is a dark brown compound, isomorphous with $UF_4$ (monoclinic crystal structure), nonvolatile under vacuum up to 800°, and virtually insoluble in water and mineral acids. Protactinium pentafluoride, $PaF_5$, is a white compound, isomorphous with the $\beta$ form of $UF_5$ (tetragonal crystal structure), soluble in aqueous hydrofluoric acid. The pentafluoride is much less volatile than its homologs $VF_5$, $NbF_5$, and $TaF_5$, but sublimes or distils under vacuum above 500°. A pentafluoride hydrate of approximate composition $PaF_5 \cdot 2H_2O$ is obtained as colorless, needle-like crystals on evaporation of solutions of protactinium in concentrated hydrofluoric acid. The hydrate decomposes at 160°, forming an oxyfluoride, $Pa_2OF_8$, which is white, isomorphous with $U_2F_9$ (body-centered cubic structure), and slightly volatile under vacuum above 500°. The oxyfluoride may also be prepared by several other methods.

## Introduction

In the earliest studies of protactinium fluorides, Grosse[2] prepared the double fluoride with potassium, $K_2PaF_7$, and a pentafluoride hydrate of unspecified composition. A double fluoride with ammonium was reported by Emmanuel–Zavizziano[3] and subsequently a double fluoride with barium was described by Golden and Maddock.[4] Sellers, Fried, Elson, and Zachariasen[5] prepared the tetrafluoride, $PaF_4$, by hydrofluorination of $PaO_2$ and reported it to be isomorphous with $ThF_4$, $UF_4$, and $PuF_4$. Haissinsky and Bouissieres[6] reduced Pa(V) in a fluoride solution and obtained a white precipitate which was also believed to be protactinium tetrafluoride.

Very little information is found in the literature concerning volatile fluorides or oxyfluorides of protactinium. Emeléus, Maddock, Miles, and Sharpe[7] heated tracer quantities of $Pa^{233}$ and $Pa^{231}$ with bromine trifluoride but found no indication that a volatile fluoride was formed. At Brookhaven National Laboratory, the distillation of tracer $Pa^{233}$ from neutron-irradiated $ThF_4$ was studied.[8] When the $ThF_4$ was strongly heated in a stream of fluorine or chlorine trifluoride, a slightly volatile protactinium compound was formed which condensed below 500°. Sellers, Fried, Elson, and Zachariasen[5] reported the formation of a volatile protactinium fluoride or oxyfluoride on heating protactinium oxide to 600° with either bromine trifluoride or bromine pentafluoride. Their product distilled under vacuum at 150° but subsequently decomposed, either by hydrolysis or reaction with the quartz vessel.

The present study reveals that a slightly volatile oxyfluoride, $Pa_2OF_8$, is formed under a variety of conditions. Several reactions useful for the preparation of the oxyfluoride, tetrafluoride, pentafluoride, and hydrated pentafluoride are reported.

## Experimental

Protactinium-231 in the form of the hydrated pentoxide was obtained from the Atomic Energy Research Establishment, Harwell, England. In most experiments, the oxide was used without further purification, since spectrographic analyses indi-

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission and the U. K. Atomic Energy Authority.

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[3] H. Emmanuel-Zavizziano, *Compt. rend.*, **202**, 1053 (1936).

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[8] F. T. Miles, R. J. Heus, and R. H. Wiswall, Jr., Report BNL 482 (T-109), Nov., 1954.