Magnetic Characteristics of Some Lanthanide Nitrides[1]

BY DAVID P. SCHUMACHER AND W. E. WALLACE

Magnetic susceptibilities (χ) of Y, La, Ce, Nd, Sm, Yb, Lu, and their nitrides were determined over a temperature range extending from 2 to 300°K. Y, La, and Lu and their nitrides are Pauli paramagnets. SmN orders antiferromagnetically below 13°K. NdN exhibits ferromagnetic ordering below 35°K. Its magnetic moment in the ferromagnetic state at 2°K is 2.15 μ_B, as contrasted with 3.3 μ_B for the free Nd^{3+} ion. The reduction is ascribed to crystal field quenching. From the measured moment an over-all splitting of the ground state Nd^{3+} ion multiplet is estimated to be 234°K. The effective moment of Nd in paramagnetic NdN is in good agreement with that expected for the free ion. YbN exhibits Curie–Weiss behavior at >100°K with a moment in fair agreement with that expected for the Yb^{3+} ion. However, the magnitude of χ for YbN and the low-temperature deviation from Curie–Weiss behavior are not understood. Results for Yb indicate 34% Yb^{3+} and 66% Yb^{2+}. The CeN results indicate a mixture of Ce^{3+} and Ce^{4+} with the latter strongly predominating at low temperatures. In accordance with theoretical expectations no magnetic ordering is observed for CeN and YbN at temperatures down to 2°K.

I. Introduction

During recent years evidence has been steadily mounting to indicate an appreciable crystal field quenching of the orbital contribution to the magnetic moment in intermetallic compounds containing lanthanides.[2,3] Neutron diffraction,[4] magnetic susceptibility,[5,6] and paramagnetic resonance[7] studies have indicated the influence of crystal field effects in the heavy rare earth nitrides. The present investigation was undertaken partly to determine the effects of crystal field quenching in several light lanthanide nitrides, as was done for PrN.[8]

There was another major reason for undertaking the present study. In the earlier work it was observed that while the susceptibility (χ) behavior of PrN and TmN was in qualitative agreement with that expected when due allowance was made for the quenching effect of the crystal field, results could not be accounted for quantitatively, as had been the case for some other systems studied, *e.g.*, PrSb and PrBi.[9] The suggestion was advanced[8] that since these nitrides are undoubtedly incompletely ionic, the aberrant results might originate with some subtle features of the $6s^2 5d$ bonding electrons. Elucidation of their role is of course facilitated in systems which are free of f electrons. It was in this general connection that work on LaN and LuN, together with chemically similar YN, was begun. In the course of the studies extension was made to include the Ce, Nd, Sm, and Yb nitrides, which

have not received attention to date at temperatures below the liquid nitrogen point.

II. Experimental Section

The best grade of lanthanide metals (99.9% by suppliers' claims)[10] were cleaned under mineral oil with a 600A corundum paper to remove surface film, rinsed in carbon tetrachloride, acetone, and ether in that order, and finally weighed under oil. The europium metal was cleaned and weighed in a drybox which was continuously flushed with argon. The cleaned samples of 0.1–2.0 g were then degassed *in vacuo* in a quartz reaction tube at 600° or at 400° if they had a tendency to sublime. To form the nitride, the samples were first hydrided by admitting approximately 1 atm of hydrogen,[11] which had been evolved from a titanium hydride bed, to the hot metal and allowing the system to cycle automatically between room temperature and 800° for several days. Prepurified N_2, which had been liquefied over sodium metal, was added to the hydride after all unreacted hydrogen remaining at room temperature was removed. The conversion of the hydride to nitride was carried out at 900–1000° for approximately 3 days. The stoichiometry of the nitride was computed from the known amounts of the metal used and the measured amounts of unreacted gases remaining after conversion.

The samples were annealed *in vacuo* at 950° to remove excess hydrogen and unreacted metal by sublimation (Eu, Sm, Ce, Yb, and La). All the nitrides were in powder form and black, except for CeN, which was dark brown.

Magnetic measurements were made by the Faraday method using a Sucksmith gap[12] and an automatic recording balance.[13] Fields up to 20 koersteds were available to measure susceptibility as a function of field at constant temperature. All thermomagnetic analyses were made at 19 koersteds. A continuous recording of the temperature was made from 4.2 to 300°K by using carbon and platinum resistance thermometers. Temperatures below 4.2°K were obtained by pumping on the liquid helium and measuring its vapor pressure. All samples were sealed in a copper sample holder fitted with a Teflon plug to prevent oxidation of the nitride. The sample holder was filled and weighed in an argon-filled box.

(1) This research was assisted by the U. S. Atomic Energy Commission.
(2) J. Farrell and W. E. Wallace, *Inorg. Chem.*, **5**, 106 (1966).
(3) See Chapter by W. E. Wallace, *Ann. Rev. Phys. Chem.*, **15**, 109 (1964), for numerous earlier references to crystal field effects in lanthanide intermetallics.
(4) H. R. Child, M. K. Wilkinson, J. W. Cable, W. C. Koehler, and E. O. Wollan, *Phys. Rev.*, **131**, 922 (1963).
(5) G. Busch, P. Junod, O. Vogt, and F. Hulliger, *Phys. Letters*, **6**, 79 (1963).
(6) B. R. Cooper, I. S. Jacobs, R. C. Fedder, J. S. Kouvel, and D. P. Schumacher, paper presented at the 11th Annual Conference on Magnetism and Magnetic Materials, 1965.
(7) R. C. Fedder, B. R. Cooper, and D. P. Schumacher, *Bull. Am. Phys. Soc.*, [2] **11**, 15 (1966).
(8) D. P. Schumacher and W. E. Wallace, *J. Appl. Phys.*, **36**, 984 (1965).
(9) T. Tsuchida and W. E. Wallace, *J. Chem. Phys.*, **43**, 2885 (1965).

(10) Obtained from Research Chemicals, Phoenix, Ariz.: Y, La, Nd; and Sm, Eu, Yb, which were purified by distillation. The lutetium was obtained from Johnson, Matthey and Co., Ltd., London, E.C. 1, England; and the cerium (99.99%) from United Mineral and Chemical Corp., New York, N. Y.
(11) The H_2 and N_2 contained less than 0.1 ppm of oxygen: F. S. Humphries, Doctoral Dissertation, University of Pittsburgh, 1964.
(12) W. Sucksmith, *Proc. Roy. Soc.* (London), **A170**, 551 (1939).
(13) R. A. Butera, R. S. Craig, and L. V. Cherry, *Rev. Sci. Instr.*, **32**, 708 (1961).

X-Ray diffraction patterns of nitrides which exhibited anomalous magnetic properties were obtained after magnetic analysis. A General Electric XRD-5 diffractometer with Mo radiation (Zr filter) was used. Peaks due to unreacted metal were not observed in any of the patterns.

III.   Results

Results are largely summarized in Figures 1–3 and in Table I. The measured susceptibilities ($\times 10^{-6}$ emu/g) of the three nonmagnetic lanthanide nitrides at various temperatures are

	4.2°K	10°K	20°K	50°K	100°K	200°K
YN	6.30	4.70	3.48	2.16	1.29	0.64
LaN	4.15	2.73	1.82	0.95	0.58	0.31
LuN	1.15	0.64	0.31	0.13	0.04	−0.04

The data corrected for the diamagnetism of N^{3-} are shown in Figure 1, together with corresponding data for portions of the three metal samples used in preparing the nitrides. Data for the other four nitrides
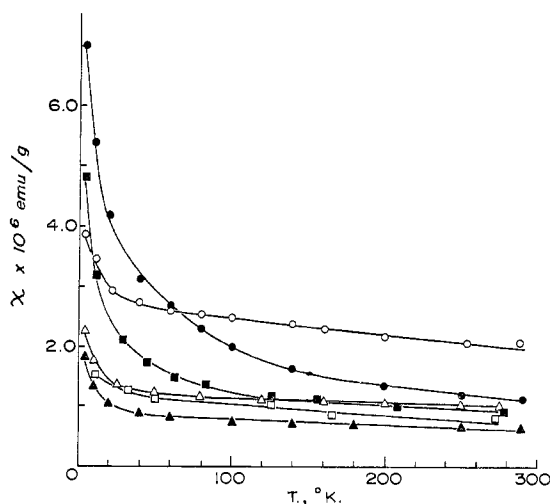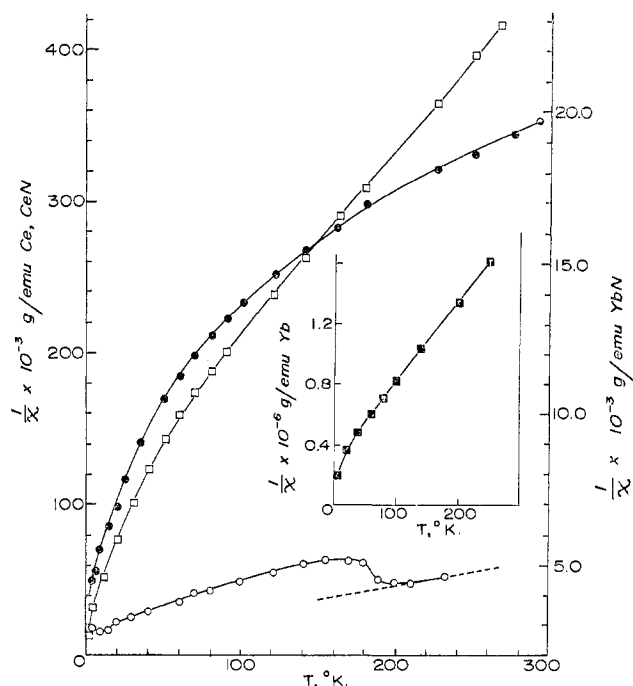

Figure 2.—Inverse susceptibilities as a function of temperature for Ce (O), CeN (●), Yb (■), and YbN (□). The dashed line represents the second thermomagnetic analysis on Ce after recooling the sample to 150°K from 240°K. The left scale is for Ce and CeN, the right for YbN.

Figure 1.—Measured susceptibilities of Y (O), La (□), and Lu (△), and the susceptibilities of YN (●), LaN (■), and LuN (▲) corrected for the diamagnetism of N^{3-} (−0.7 × 10^{-6} emu/g).

are shown in Figures 2 and 3. The results indicate ordering for NdN (ferromagnetic) and SmN (antiferromagnetic) below 35 and 13°K, respectively. There is no indication of ordering in the other nitrides, even for temperatures down to 2°K.

Several of the paramagnetic nitrides exhibited χ values at 4.2°K which varied with field strength, decreasing as field strength is increased. With LaN, LuN, and YN the over-all change was small (about 10%) and is probably due to impurities. Around 10 ppm of ferromagnetic impurity would produce the observed effect. The field dependency for the Ce and Yb nitrides is somewhat larger and is probably an intrinsic characteristic of these substances— the saturating effect of high fields at these low temperatures. Elemental cerium exhibits very pronounced hysteresis effects in χ (and in other properties) on thermal cycling.[14] CeN is free of this effect, although it shows a small amount of isothermal hysteresis at 2°K. Its susceptibility is about 4% larger as measured with

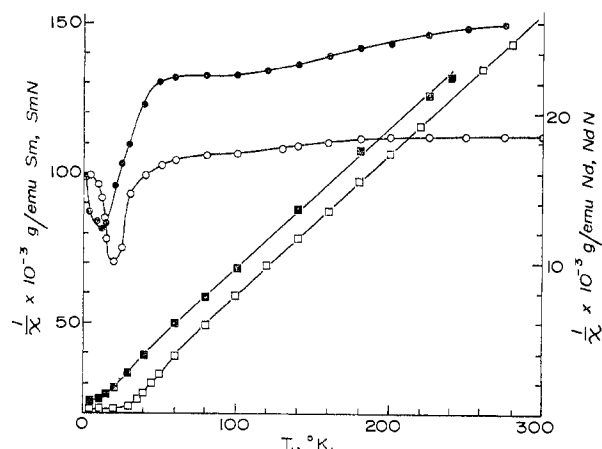(14) J. M. Lock, *Proc. Phys. Soc.* (London), **70B**, 566 (1957).

Figure 3.—Inverse susceptibilities of Sm (O), SmN (●), Nd (■), and NdN (□) as a function of temperature. The left scale is for Sm and SmN, the right for Nd and NdN.

decreasing field over that observed with increasing field. This is probably due to enhancement and subsequent retention of the magnetic Ce^{3+} compound (*vide infra*) at large applied fields.

Attempts were made to prepare EuN for study. These were unsuccessful due to extensive oxide inclusion, presumably brought about by reaction with the quartz container tube.

Magnetization-field measurements for NdN at 2°K gave a saturation moment of 2.15 μ_B. At temperatures in excess of 80°K Curie–Weiss behavior was observed for Nd and Yb and their nitrides. Paramagnetic moments computed from the slopes of the curves in the linear region of $1/\chi$ vs. T are given in Table I. The

TABLE I

MAGNETIC CHARACTERISTICS OF LANTHANIDE METALS AND THEIR NITRIDES

	$\chi_M{}^{296}$	$\chi_M{}^{4.2}$	T_N, °K	T_0, °K	$\theta_p{}^a$	Effective moment at 296°K, μ_B/formula unit	
	emu/mole $\times$ 10^6					Exptl	Calcd^b
Ce	2190	8,580	...	...			
CeN	433^d	3,160	...	...			
Nd	5260	205,000	...	...	−5	3.54	3.68
NdN	6060^d	555,000	...	35	15	3.70	3.68
Sm	1340	1,520	20	...	...		
SmN	1070^d	1,870	13	...	...		
Yb	94	953	...	...	−55	0.52 (0.41)^c	0 (Yb^{2+})
YbN	7590^d	62,000	...	...	−102	4.93	4.5
Y	178	344					
YN	45	648					
La	111	Superconductor below 6°K, $\chi_M{}^{4.2}$ = −180 $\times$ 10^{-6}					
LaN	38	634					
Lu	175	393					
LuN	120,^{e} −151	331					

^{a} The Néel temperature (T_N), Curie temperature (T_c), Weiss constant (θ_p), and the molar susceptibilities are for fields of 19 koersteds. ^{b} The calculated moment is that for Ln^{3+} unless otherwise indicated. ^{c} K. A. Gschneidner, "Rare Earth Alloys," D. Van Nostrand Co., Inc., New York, N. Y., 1961, p 42. ^{d} These values are in good agreement with those given by R. Didchenko and F. P. Gortsema, *J. Phys. Chem. Solids*, **24**, 863 (1963). ^{e} Corrected for the diamagnetism of N^{3-}.

non-Curie–Weiss behavior for Sm and SmN is as expected. As pointed out by Van Vleck,[15] this is a consequence of the narrowness of the multiplet structure for Sm and has been observed for other Sm compounds investigated in this laboratory.[9,16]

IV. Discussion of Results

(A) Y, La, and Lu and YN, LaN, and LuN.—These nitrides are ones in which the metallic ion does not carry a magnetic moment. This is also true for the parent metals, of course. The latter are regarded as Pauli paramagnets, *i.e.*, substances in which the susceptibility is primarily due to the conduction electrons. The Pauli susceptibility is virtually independent of temperature. It is seen from Figure 1 that χ for the three nitrides and the parent metals exhibits some variation with temperature, although the extent is much less than the 75-fold variation expected from Curie's law. The increase for the pure metals for T <50°K is probably an impurity effect; 0.001% of the strongly magnetic lanthanides (Gd, Dy, etc.) present in solid solutions would account for the increment in χ. Thus, the results obtained for Y, La, and Lu support the viewpoint that they are simple Pauli paramagnets.

The situation for the nitrides is similar to that for the metals. There is variation of χ with temperature, but it is slight compared to that expected for an ion carrying a moment, and therefore it can be assumed that the nonmagnetic nitrides are Pauli paramagnets similar to their parent metals. However, the low-temperature rise in χ for the nitrides exceeds that for the metals, suggesting that part of the temperature dependence must be intrinsic—perhaps a property of the partial covalency of these metals.

Since the Pauli susceptibility is proportional to the density of states, one would expect χ for the nitride (corrected for N^{3-} diamagnetism) to be less than that

of the metal due to loss of conduction electrons by N^{3-} ion formation. This is the case for LuN and for YN above 60°K but not for YN at lower temperatures or for LaN. The size of the χ values for LaN and YN, as compared to those for La and Y, is not as yet understood.

It was pointed out above that one reason for examining the nitrides of Y, La, and Lu was to ascertain the low-temperature magnetic behavior of nitrides which lack f electrons and to establish whether these results provide a clue as to the origin of the aberrant susceptibility–temperature behavior of PrN and TmN. The present data clearly indicate a contribution to χ which depends on temperature, but the magnitude of the variation is far too small to account for the peculiar results obtained for TmN and PrN.

(B) Crystal Field Effects in the Lanthanide Nitrides.—Before discussing the results obtained for the substance in which the lanthanide ion carries a moment it is desirable to elaborate upon the general effects of the crystal held in regard to the bulk magnetic characteristics—susceptibilities and saturation magnetizations—of these nitrides. Comments are limited to NdN and YbN in view of the discussion to follow. These nitrides have the rock-salt structure. The crystal field in this case splits the ground-state multiplet into a ground-state doublet in both cases and excited states consisting of two quartets for Nd^{3+} and a quartet and a doublet for Yb^{3+}, the latter being the highest energy state.[17] From other studies[2] it can be assumed that the splitting is sufficiently large that a substantial rearrangement of the level population occurs on cooling into the liquid helium range. For zero or small splitting and where the levels are statistically populated, the effective ion moments (in μ_B) in the paramagnetic and ferromagnetic regions are very nearly $g\sqrt{J(J+1)}$ and gJ. However, for appreciable splitting the levels are no longer statistically populated and the ferro-

(15) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, New York, N. Y., 1932, p 248.
(16) Y. Kubota and W. E. Wallace, *J. Appl. Phys.*, **34**, 1348 (1963).

(17) K. R. Lea, M. J. M. Leask, and W. P. Wolf, *J. Phys. Chem. Solids*, **23**, 1381 (1962).

magnetic moment measured at the lowest temperatures is that of the ground-state doublet. Furthermore, the effective paramagnetic moment varies with temperature as repopulation of the levels takes place. As a result of the varying moment significant deviations from Curie–Weiss behavior begin to occur when there begins to be deviation from statistical population of the crystal field levels. This latter effect was discussed many years ago in the classic paper of Penney and Schlapp,[18] in which it is shown that in cases such as NdN and YbN, where the ground state is a doublet, negative deviations from Curie–Weiss behavior set in. The details of the $1/\chi$ vs. temperature curve can be calculated[18] in terms of a crystal field parameter, which Penney and Schlapp called a, and from this a the particulars of the crystal field spectrum are obtained.

The moment in a ferromagnetic material can also be obtained. Referring to NdN at low temperatures the ions are essentially all in the doublet state. Their moment can be calculated by perturbation theory. Penney and Schlapp worked this out for Nd^{3+} and obtained for μ the moment/ion in μ_B.

$$\lambda = 1.83g + 0.1412g^2\mu_B H/a$$

where H is magnetic field, g is the Landé factor, μ_B is the Bohr magneton, and a is the crystal field parameter. There is thus a permanent and an induced moment. The expression obtained by Penney and Schlapp, and later by Schumacher and Hollingsworth[19] for Yb^{3+}, is a limiting form for low fields. For high fields, such as the molecular field in NdN, the determinant obtained from perturbation theory must in some cases be solved more exactly, but the principle is the same. In the ferromagnetic case the Curie temperature is used to estimate the molecular field and this is used to establish the total field acting on an ion which is involved in the determinant. The measured moment can then be used to evaluate the parameter a, from which the over-all splitting and the energy of the first excited state can be obtained.

(C) The Nitrides of the Magnetic Lanthanides. Behavior in the Paramagnetic Region.—In this region three effects may be involved: (1) the narrowness of the multiplet spacing (Sm in SmN), referred to above, (2) the influence of the crystal field (NdN and YbN), and (3) valence changes (CeN, Yb, and YbN).

As regards SmN (and Sm) Van Vleck and Frank[20] have pointed out that the moment is temperature dependent and can be computed from χ at temperature from the equation

$$\mu_{\rm eff} = 2.83\sqrt{\chi_M T}$$

The $\mu_{\rm eff}$ values for Sm^{2+} and Sm^{3+} at 296°K are 3.45 and 1.60 μ_B, respectively. The measured values are 1.79 μ_B for Sm (as compared with 1.74 quoted by Gschneidner)[21] and 1.60 μ_B for SmN at 296°K. These

(18) W. G. Penney and R. Schlapp, *Phys. Rev.*, **41**, 194 (1932).
(19) D. P. Schumacher and C. A. Hollingsworth, *J. Phys. Chem. Solids*, **27**, 749 (1966).
(20) J. H. Van Vleck and A. Frank, *Phys. Rev.*, **34**, 1494 (1929).
(21) K. Gschneidner, "Rare Earth Alloys," D. Van Nostrand Co., Inc., New York, N. Y., 1961, p 42.

results confirm the tripositive nature for Sm in the element and in its nitride, agreeing in the latter case with inferences which can be drawn from crystallographic data.

The nonlinearity of the $1/\chi$ vs. T data for CeN is attributed to a change in valence, analogous to that observed for the element.[14] The steadily increasing slope with decreasing temperature can be formally identified with a decrease in magnetic moment per Ce ion. Tripositive Ce has a $\mu_{\rm eff}$ of 2.56 μ_B whereas $\mu_{\rm eff}$ for Ce^{4+} is zero. The steady decrease in moment implies a progressive increase in the Ce^{4+} component in CeN as temperature is lowered. The high concentration of nonmagnetic Ce is undoubtedly responsible in part for the lack of magnetic ordering in this material at 2°K.

As mentioned above, when there is an appreciable crystal field effect and when the ground crystal field state is a doublet, the $1/\chi$ vs. T plot shows negative deviations from linearity. The extent of the deviation is related to the Penney–Schlapp crystal field parameter, a. NdN and YbN, whose ground states are doublets, show the expected negative deviations. In principle the a parameter can be evaluated from the extent of the deviation. In practice this cannot be done at least with any degree of reliability for NdN because ferromagnetism sets in at a fairly high temperature, before the deviations become large enough to use. The behavior of NdN in the paramagnetic region is clearly in qualitative agreement with expectation.

Attempts were made to estimate a for YbN. These were unsuccessful. The χ values were too low to be accounted for by any value of a. This feature is reflected in the large negative value of the Weiss constant. It is clear that some factor operates to produce an anomalously low χ for this nitride. A large negative Weiss constant (θ) usually implies strong antiferromagnetic interactions and the onset of antiferromagnetic ordering at fairly high temperatures. The lack of ordering down to 2°K in YbN indicates that this line of reasoning is inapplicable here. The other factor which can give a low χ and a large negative θ is a mixture of valencies, $+2$ and $+3$ in this case. If a considerable fraction of Yb in YbN is in the nonmagnetic $+2$ state, a diminished χ is expected. If so, a moment intermediate between that for Yb^{2+} and Yb^{3+} is anticipated. Actually, the moment for $T < 100°K$ is slightly larger than that expected for the tripositive state. The negative deviations in the $1/\chi$ vs. T curve below 100°K could be due to crystal field quenching or a valence change or a combination of these two effects. However, the magnitude of χ and the slope of the $1/\chi$ vs. T curve in the Curie–Weiss region are not consistent with these possibilities. The factors responsible for the peculiar behavior of YbN are as yet not clear.

The results for CeN seem fairly straightforward. The increasing slope at reduced temperatures in the $1/\chi$ vs. T plot for this compound (Figure 3) indicates a steadily decreasing moment. This is clear indication

of an increasing fraction of nonmagnetic Ce^{4+} brought on by thermal contraction.

The effective moment for Yb (Table I) is 0.52 μ_B, much smaller than the value for Yb^{3+} (4.5 μ_B). This moment can be formally regarded as due to a mixture of 34% Yb^{3+} and 66% Yb^{2+} ions.

Behavior in the Region of Magnetic Ordering.— Two aspects of this phase of the work merit comment— the lack of ordering in YbN and CeN and the magnitude of the moment in NdN. As regards the former, the interactions in lanthanide systems are proportional to the de Gennes[22] function $(g - 1)^2 J(J + 1)$. Since the ordering temperatures parallel the magnitude of the interactions, the expected Néel or Curie temperatures for CeN and YbN can be estimated from

(22) P. G. de Gennes, *Compt. Rend.*, **247**, 1836 (1958).

the known ordering temperature of another LnN, *e.g.*, GdN. They are both calculated to be less than 1°K, which accounts for the nonobservance of ordering in these materials in the present work.

The low moment measured for NdN is ascribed to the quenching effect of the crystal field. At 2°K the Nd^{3+} ions are in the doublet ground state. Using the reasoning outlined above the Penney–Schlapp *a* parameter can be evaluated for ferromagnetic NdN using 2.15 μ_B, the measured moment. *a* is calculated to be 2.34 × 10^{-16} erg or 1.17 cm^{-1}. Thus the first excited level is at 76°K and the over-all splitting is 234°K. These are in the same range as the values observed for PrSb and PrBi–59 and 52°K, respectively, for the energy of the first excited level and 226 and 201°K, respectively, for the over-all splitting.

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The Preparation and Some Properties of $Nd_2O_2C_2$[1]

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The results of hydrolysis experiments, X-ray powder diffraction data, and some thermodynamic properties of a phase in the neodymium–oxygen–carbon system of the approximate composition $Nd_2O_2C_2$ are reported.

Introduction

The reported presence of oxygen in uranium dicarbide preparations[3] and reports of a U(O,C) phase[4] establish the existence of ternary carbon–oxygen–metal phases. Since the dicarbide of uranium is structurally similar to those reported for lanthanide elements, such ternary phases are to be expected among the lanthanides. Recently, the probable existence of the phases Y_2C_2O and Sc_2C_2O has been reported.[5,6] This work was undertaken to examine the Nd–O–C system. The preparation and some properties of a ternary phase, $Nd_2O_2C_7$, are reported below.

Experimental Section

Preparation.—Two different preparatory procedures were followed. In the first of these, weighed quantities of calcined 99.9% pure neodymium sesquioxide (Michigan Chemical Co., St. Louis, Mich.) and either Acheson grade No. 38 graphite powder (Fisher Scientific Co.) or crushed spectrographic rods were ground together in the ratio of 1 mole of the sesquioxide to

(1) Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

(2) Abstracted in part from the Master's Thesis of G. L. Buchel, submitted to the College of Natural Science of Michigan State University.

(3) C. B. Alcock, H. A. Eick, E. G. Rauh, and R. J. Thorn in "Nuclear Metallurgy," Vol. X, J. T. Waber, P. Chiotti, and W. N. Miner, Ed., Edwards Bros., Ann Arbor, Mich., 1964, p 257.

(4) R. F. Stoops and J. V. Hamme, *J. Am. Ceram. Soc.*, **47**, 59 (1964).

(5) G. V. Samsonov, T. Ya. Kosolapova, M. D. Lyutaya, and G. N. Makarenko, *Redkozem. Elementy Akad. Nauk SSSR, Inst. Geokhim. Analit. Khim.*, 8 (1963).

(6) T. Ya. Kosolapova and G. N. Makarenko, *Redkie i Redkozem. Elementy v Tekhn. Akad. Nauk Ukr. SSR, Inst. Probl. Materialoved.*, 94 (1964); *Chem. Abstr.*, **62**, 8561c (1965).

between 3 and 7 moles of graphite. The mixture was pressed into cylindrical pellets 0.6 cm in diameter and 1.4 cm in height at a pressure of about 2500 psi. Two pellets were centered into a previously outgassed graphite reaction crucible which was machined with a snugly fitting lid through which an 0.8-mm diameter hole had been drilled. This hole permitted the escape of gases and provided a line of sight for measurement of the cavity temperature. The crucible assembly sat on a 19 mm high graphite stand, of diameter equal to that of the crucible, supported by three 2.5-mm diameter tungsten or graphite legs. The inductively heated crucible assembly sat on a boron nitride support. A water-cooled Vycor heating tube equipped with an optical window at its top surrounded the crucible and its charge and permitted a pressure of approximately 10^{-5} torr to be attained in the tube. Temperatures were measured with a Leeds and Northrup disappearing-filament type of optical pyrometer calibrated at the National Bureau of Standards. All temperatures have been corrected for optical window (and prism) absorption errors. Since reaction did not proceed below 1350°, the reactants were outgassed by heating the loaded crucible at 1000° until the system exhibited a constant pressure, as measured with a stainless steel absolute-pressure type of Wallace and Tiernan factory-calibrated manometer (Model FA-145). Heating was then suspended and the system was reevacuated. Subsequently, the temperature of the system was elevated quickly to the desired operating temperature where it was maintained for 3.5–5 hr. After the product had cooled, it was removed and examined by X-ray powder diffraction to check for the presence of neodymium sesquioxide. If any was observed, it was removed by reheating the pellets and pumping off some of the carbon monoxide produced as a result of reaction. Usually two such pump-offs were required for a 3-g sample. Each time, the pellet was removed from the crucible and placed quickly into a glove box filled with dried helium.