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Magnetic Susceptibilities of Praseodymium Oxides*

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The magnetic susceptibilities of the three oxides of praseodymium, Pr2O₃, PrO₂, and Pr₆O₁₁, have been measured with the faraday magnetic balance over a range of temperatures from 80° to 300°K. The sesquioxide and the dioxide have been found to have moments of 3.55 and 2.48 Bohr magnetons, respectively, and to obey the Weiss modification of the Curie law, $\chi(T+\Delta) = C$, over the range of temperatures studied with corresponding values of Δ equal to 55.0° and 104°. A curvature was noted in the plot of $1/\chi$ vs T for the oxide Pr₆O₁₁. Thus the Weiss-Curie law does not adequately express the relationship between the susceptibility and the temperature for this oxide. A moment of 2.8 Bohr magnetons was calculated for Pr_6O_{11} from the slope of the above plot between 200° and 300°K.

INTRODUCTION

N spite of the large number of investigations of the magnetic properties of the rare earths, relatively few measurements have been made on the oxides of praseodymium as a function of temperature. Selwood¹ apparently overlooked the work of Cabrera and Duperier² and that of Klemm and Koczy,³ for he estimated a value for the gram susceptibility of the sesquioxide of praseodymium. To the author's knowledge no susceptibility data have been reported for the oxide Pr₆O₁₁ as a function of temperature, and only Cabrera and Duperier² appear to have measured PrO_2 in this manner.

Susceptibility measurements have been made on analyzed samples of the three oxides of praseodymium, Pr₂O₃, Pr₆O₁₁, and PrO₂ over a range of temperatures from 80° to 300°K.



* This work was done under the auspices of the AEC. ¹ P. W. Selwood, Magnetochemistry (Interscience Publishers, Inc., New York, 1943), p. 232. ² B. Cabrera and A. Duperier, Compt. rend. 188, 1640 (1929).

³ W. Klemm and A. Koczy, Z. anorg. Chem. 233, 84 (1937).

EXPERIMENTAL

The susceptibilities were measured by the vertical force method with a faraday magnetic balance. The apparatus was assembled by Lewis and Elliott.⁴ The magnet and the power supply were manufactured by the Consolidated Engineering Corporation of Pasadena, California. An Ainsworth type TCX semimicro balance was used to measure the force exerted on the sample. A phosphor-bronze capsule of the type shown in Fig. 1 was used to contain the specimen under investigation. The mapping of the field to locate the region of maximum HdH/dx was accomplished by reading the position of the capsule relative to a fixed reference point by means of a Gaertner cathetometer. The temperature of the sample was measured with copperconstantan thermocouples which had been checked against a platinum resistance thermometer certified by the Bureau of Standards.

The phosphor-bronze capsule was surrounded by a copper tube which was placed inside a silvered Pyrex glass Dewar flask. Around the copper tube was placed a copper spiral coil through which liquid nitrogen was pumped. The desired temperature was achieved by a proper selection of the length of the pump stroke and the number of strokes per minute. The emf of the controlling copper-constantan thermocouple was opposed with a Rubicon precision potentiometer. The condition of unbalance was indicated by a Leeds and Northrup moving coil, reflecting galvanometer, and the reflected light beam was projected on a photoelectric cell which activated the relay controlling the operation of the liquid nitrogen pump. With this assembly the temperature of the copper tube surrounding the phosphorbronze capsule could be controlled to within a few tenths of a degree. Additional details of the apparatus will be found in the paper of Lewis and Elliott.⁴

The rare earth sample was obtained in the form of the oxide, Pr₆O₁₁, from Professor F. H. Spedding at the Institute for Atomic Research, Ames, Iowa. A spectrographic analysis of this oxide indicated 0.005 percent magnesium, and the quantities of other rare earths

⁴ W. B. Lewis and N. Elliott (to be published).

present were beyond the limit of detection. The absence of ferromagnetic impurities in the oxide was demonstrated by measuring the susceptibility as a function of the magnetic field strength.

The oxide Pr₂O₃ was prepared by inductively heating Pr₆O₁₁ at a temperature of about 1400° for sixteen hours at a pressure of about 5 microns. An x-ray analysis of this sample showed it to be the A (hexagonal) form of Pr₂O₃. No other component was indicated by the x-ray diffraction pattern.

Pr₆O₁₁ was prepared for the magnetic measurement by heating the sample as received for one hour in air at approximately 1000° in a platinum crucible to remove any moisture and to decompose any carbonates which might have formed. The resulting oxide was shown by its x-ray pattern to consist of a single component.

The method of McCullough⁵ was used in the preparation of PrO₂. This procedure consisted of heating the oxide Pr₆O₁₁ to 300° for 48 hours under a pressure of 60 atmospheres of oxygen in a quartz capillary. Again an x-ray diffraction pattern of this material failed to reveal the presence of a second component. The lattice constants of Pr_6O_{11} and of PrO_2 are in agreement with those obtained by McCullough,⁵ while those for Pr₂O₃ are in accord with the results of Eyring, Cunningham, and Lohr⁶ for the A form of this oxide. The "active oxygen" method of analysis developed by Barthauer and Pearce⁷ was used to serve as an additional check on the composition of the praseodymium oxides. Whereas the theoretical percentages of "active oxygen" are 0.0, 3.13, and 4.63 for the oxides Pr_2O_3 , Pr_6O_{11} , and PrO_2 , respectively, the experimentally observed percentages were 0.0, 3.14, and 4.7. The latter value is within the experimental error because of the limited sample.

The magnetic balance was calibrated with potassium chrome alum as the standard of susceptibility, and the values obtained by de Haas and Gorter⁸ were used for this salt. A crystal of manganous sulfate tetrahydrate was measured over the range of temperature from 80° to 300°K as a check on the reliability of the calibration. A linear relation between $1/\chi$ and T was obtained. A moment of 5.86 Bohr magnetons was obtained for this salt, and the absolute values of the susceptibility were within approximately 1 percent of the values obtained by Tackson.9

The contribution of the empty phosphor-bronze capsule was measured as a function of temperature. This blank was also measured both before and after each measurement. The phosphor-bronze capsule was loaded with the oxide samples in an inert "drybox"

TABLE I. The susceptibility of praseodymium sesquioxide as a function of temperature.

<i>T</i> , ⁰K	xg ×10⁴	$X'_M \times 10^6$	X _M ×10 ⁴	1/x _M ×10 ⁻¹
297.9	26.80	4420	4478	2.233
263.4	29.63	4887	4945	2.022
243.4	31.67	5223	5281	1.894
215.6	34.84	5746	5804	1.723
182.3	39.60	6530	6588	1.518
149.2	46.58	7681	7739	1.292
83.3	68.87	11358	11416	0.876

to prevent the reaction of either carbon dioxide or moisture with the sample.

EXPERIMENTAL RESULTS

In Table I are given the values for the susceptibility per gram of Pr_2O_3 , χ_g , and the susceptibility of Pr_2O_3 per gram atom of praseodymium as a function of temperature. A correction of -58×10^{-6} was applied for the diamagnetism of the oxide. In calculating the diamagnetic correction to be applied, a value of -13×10^{-6} was used as the contribution of the oxygen and -38×10^{-6} was used for the rare earth ions in all three oxides. The latter value is that given by Pauling¹⁰ for La+++. While both Pr+++ and Pr++++ have 4f electrons, whereas La+++ does not, it is believed that the diamagnetic corrections for these rare earth ions are approximately correct, since, as Van Vleck11 has stated, the electrons in the 4f shell contribute less to the diamagnetism than the surrounding 5s and 5p shells. The values of the susceptibility of Pr₂O₃ in Table I are approximately 2 to 3 percent less than the values of Cabrera and Duperier² and Velayos,¹² and 3 percent greater than the values of Klemm and Koczy.³ The susceptibility of Pr₂O₃ can be satisfactorily represented by the Weiss-Curie law from 80° to 300°K. A moment of 3.55 Bohr magnetons was calculated for this oxide and a value of 55.0° was found for Δ , the molecular field constant. The moment was calculated from the relation $\mu = 2.83 [\chi(T+\Delta)]^{\frac{1}{2}}$. The χ' values have not had the diamagnetic correction for the ions applied.

The Weiss-Curie law has also been found to express adequately the relation between the susceptibility and temperature for the oxide PrO₂. See Table II. A correction of -64×10^{-6} was applied to the measured results

TABLE II. Susceptibility-temperature relation for PrO₂.

<i>Τ</i> , °K	$\chi_g imes 10^6$	$\chi'_M \times 10^6$	$\chi_M imes 10^6$	$1/x_M \times 10^{-1}$
298.6	10.75	1858	1922	5,203
267.9	11.53	1994	2058	4.859
242.2	12.50	2162	2226	4.492
201.6	14.17	2450	2513	3.979
174.4	15.62	2700	2764	3.618
82.9	23.44	4052	4116	2.430

L. Pauling, Proc. Roy. Soc. (London) 114A, 181 (1927).
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 S. Velayos, Anales españ. fís. quím. 33, 5 (1935).

⁸ J. D. McCullough, J. Am. Chem. Soc. **72**, 1386 (1950). ⁹ Eyring, Cunningham, and Lohr, UCRL-791, July (1950). ⁷ G.L. Barthauer and D. W. Pearce, Ind. Eng. Chem., Anal. Ed.

<sup>18, 479 (1946).
&</sup>lt;sup>8</sup> W. J. de Haas and C. J. Gorter, Proc. Acad. Sci. Amsterdam
33, 676 (1930).
⁹ L. C. Jackson, Proc. Roy. Soc. (London) A140, 704 (1933).



FIG. 2. Reciprocal of the magnetic susceptibility of the praseodymium oxides as a function of temperature. (A) PrO_2 , (B) Pro_{211} , (C) Pr_2O_3 . --- Celayos; --- Cabrera and Duperier; --- Klemm and Koczy; --- Co-- This investigation.

for the diamagnetism of the ions. A moment of 2.48 Bohr magnetons and a Δ value of 104° were found for PrO₂. A comparison of the results of the present work with that of other investigators is given in Fig. 2.

The susceptibility-temperature relationship for the oxide Pr_6O_{11} is not adequately expressed by the Weiss-Curie law over the temperature range studied. Measurements on four independent samples of Pr_6O_{11} with an average weight of 30 mg gave concordant results for the susceptibilities of this oxide. Since a plot of $1/\chi$ vs T shows a definite curvature, no attempt was made to calculate a value for the molecular field constant. A moment of 2.8 Bohr magnetons was calculated for the oxide Pr_6O_{11} from the slope of the above plot in the temperature range between 200° and 300°K. A diamagnetic correction of -62×10^{-6} has been applied to the susceptibility values per gram atom of rare earth as given in Table III.

DISCUSSION

The experimentally observed moment of 3.55 Bohr magnetons obtained for Pr^{+++} is in good agreement with the results of other investigators (Fig. 2) and with the theoretical value of 3.62 calculated by Van Vleck and Frank.¹³ Cabrera and Duperier² stated that the oxides Pr_2O_3 and PrO_2 do not conform to the Weiss-Curie law and proposed the formula $(\chi+k)(T+\Delta)=C$ as best representing the susceptibility-temperature relationship for these oxides. Their values for the Curie con-

¹³ J. H. Van Vleck and A. Frank, Phys. Rev. 34, 1494, 1625 (1929).

TABLE III. Susceptibility of Pr₆O₁₁ as a function of temperature.

<i>т</i> , °К	xg×10 ⁶	$\chi'_M imes 10^6$	$x_M imes 10^6$	$1/x_M \times 10^{-2}$
299.3	14.30	2435	2494	4.010
272.2	15.27	2600	2659	3.761
256.9	15.91	2709	2768	3.589
241.4	16.65	2835	2894	3.455
215.9	18.11	3083	3142	3.183
184.7	20.23	3444	3503	2.855
150.4	23.83	4057	4116	2.430
130.9	26.67	4540*	4599	2.174
118.9	28.56	4862*	4921	2.032
105.5	31.51	5365*	5424	1.844
80.8	38.50	6555*	6614	1.512

* Independent sample.

stant, C, for these two oxides were 1.617 ± 0.005 and 0.861 ± 0.010 , respectively. However, in this study it has been found that between 80° and 300°K the Curie-Weiss relation, $\chi(T+\Delta)=C$ satisfactorily represents the susceptibilities of Pr_2O_3 and of PrO_2 as a function of temperature. Values of 1.575 ± 0.004 and 0.769 ± 0.002 were found for the Curie constants of the sesquioxide and the dioxide, respectively.

Van Vleck and Frank¹³ have calculated that Ce⁺⁺⁺ should possess a moment of 2.56 Bohr magnetons. According to the Sommerfeld-Kossel rule, since Pr⁺⁺⁺⁺ is isoelectronic with Ce⁺⁺⁺, the moments of the two ions should be very nearly equal. The experimental value of 2.48 Bohr magnetons obtained for Pr⁺⁺⁺⁺ is in satisfactory agreement with this prediction. Since Cabrera and Duperier² did not report on the purity of their preparation of PrO₂, it is believed that their susceptibility measurements of this oxide are approximately 9 percent too large at room temperature.

A departure from the Weiss-Curie law was observed for the oxide Pr_6O_{11} as evidenced by the curvature of the $1/\chi$ vs T plot shown in Fig. 2. A moment of 2.8 Bohr magnetons was calculated for this oxide from the slope of the above plot in the temperature range of 200° to 300° K, since in the high temperature region the uncertainty in the molecular field constant is less important in calculations of the moment. It is not possible to distinguish between the formulas $Pr_2O_5 \cdot 2Pr_2O_3$ and $Pr_2O_3 \cdot 4PrO_2$ which have been proposed for the composition of the oxide Pr_6O_{11} from the magnetic moments of the trivalent and the tetravalent praseodymium ions, since nearly identical calculated moments of about 2.86 Bohr magnetons are found for each of the proposed formulas.

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