



## Concerning the Magnetic Susceptibility of Praseodymium Oxides

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 $H_3O^+$  involving a following rapid nonadiabatic *electron* tunneling to the activated H<sub>3</sub>O<sup>+</sup> ion with adsorption of the resulting neutral H atom, and not by "proton" transfer. This mechanism would be distinct from a complete proton transfer type of process to the negative metal surface where the proton could largely retain its identity in the surface of the metal, e.g., as is the case for electrochemical transfer into a Pd cathode. The

latter type of process is more exactly analogous to acid-base proton transfer to an anion.

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## Concerning the Magnetic Susceptibility of Praseodymium Oxides

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Polycrystalline specimens of the compound PrO2 were prepared at high oxygen pressures (200-2000 atm). The phase so formed appears to be antiferromagnetic with a Néel temperature at 14°K. In contrast to this, measured susceptibilities of PrO2 prepared at lower oxygen pressures are reported to indicate the absence of cooperative effects. Phase relations of the system praseodymium-oxygen are examined to explain the discrepancy between the two data.

RECENT article by Kern<sup>1</sup> has reported magnetic A susceptibility measurements on polycrystalline samples of the separate phases: PrO<sub>1.50</sub>, PrO<sub>1.72</sub>, PrO<sub>1.83</sub>, and PrO<sub>2.007</sub> at temperatures from 4.2° to 300°K. The measured values for PrO<sub>1.50</sub>, PrO<sub>1.83</sub>, and PrO<sub>2.007</sub> were in excellent agreement with those of previous investigators.<sup>2,3</sup> The Curie-Weiss law was found to hold over the upper portion of the temperature range investigated, and the magnetic moments were found to be close to the theoretical values predicted for the free ion. Measured susceptibilities and their temperature dependence were alleged to indicate the absence of cooperative effects, even though a discontinuity appeared in the inverse magnetic susceptibility vs temperature curve for the compound PrO<sub>2.007</sub>.

The present authors have completed a similar study for the compounds PrO<sub>1.50</sub>, PrO<sub>1.83</sub>, and PrO<sub>2.0</sub> at temperatures from 1.4° to 300°K. We find close agreement with the results reported by Kern except in the case of PrO<sub>2.0</sub>, where the curve of magnetization vs temperature shows this phase to be antiferromagnetic with the Néel temperature at 14°K. In the following, the magnetic data for PrO<sub>2.0</sub> are presented and the phase relations of the system Pr-O are discussed in an attempt to find an explanation for the discrepancy between this and the previous work.

The praseodymium dioxide measured in the present case was prepared from 99.9% pure praseodymium oxide powder obtained from the Michigan Chemical Company. The oxide was first heated at 700°C for 16 h to produce a dehydrated and well-crystallized form of PrO<sub>1.83</sub> for use as a starting material. Polycrystalline PrO<sub>2</sub> was subsequently obtained by equilibration of this material at  $351\pm3$ °C and  $225\pm10$  atm of commercial oxygen for 68 h. The specimen was first



FIG. 1. Curves of magnetization  $(\sigma_q)$  and reciprocal susceptibility  $(\chi^{-1})$  vs temperature for PrO<sub>2</sub>.

quenched to room temperature, then pressure was rapidly reduced to 1 atm.

The material produced in this manner was x-rayed using  $CrK\alpha$  radiation and was found to be single-phase PrO<sub>2</sub>. Debye-Scherrer photographs were used to accurately determine d spacings from which the cell constant  $(a_0)$  was calculated by the least-squares refinement of Mueller, Heaton, and Miller.<sup>4</sup> The value determined was  $5.392 \pm 0.001$  Å. (Actually this refinement gives a value of  $5.3922 \pm 0.00009$  Å but experience

<sup>4</sup> M. H. Mueller, L. Heaton, and K. T. Miller, Acta Cryst. 13, 828 (1960).

<sup>&</sup>lt;sup>1</sup> S. Kern, J. Chem. Phys. **40**, 208 (1964). <sup>2</sup> R. C. Vickery and A. Ruben, J. Chem. Soc. **1959**, 510. <sup>3</sup> S. W. Rabideau, J. Chem. Phys. **19**, 874 (1951).



FIG. 2. Pressure-temperature relations for the higher oxides of the system  $Pr-O_2$ .

indicates that random errors, involving measurement of the photograph, etc., give rise to a much larger error limit.) The oxygen content of the specimen was determined by the procedure described by Simon and Eyring,<sup>5</sup> who measured the weight loss resulting from reduction at 600°C in hydrogen. Within the limits of experimental error (0.01 mole of oxygen/mole of sample) the material was stoichiometric. Spectrochemical analysis of the specimen failed to detect the presence of magnetic impurities (Fe, Ni, Co). This requires the concentration of Fe and Ni be less than 50 ppm (by weight), and Co less than 100 ppm.

Magnetization measurements were made from room temperature to 1.4°K using a pendulum magnetometer described previously.<sup>6</sup> Measurements were made at a field of 15 300 Oe. Curves representing the magnetization per gram  $(\sigma_q)$  as well as reciprocal susceptibility per gram  $(\chi^{-1})$  as a function of temperature (T) are shown in Fig. 1. A peak in magnetization is evident at 14°K. At higher temperatures the Curie-Weiss law  $\chi = C/(T+\theta)$  (where  $\chi$  is the molar susceptibility; C, the Curie constant; T, the temperature in Kelvin degrees; and  $\theta$ , the Weiss constant also in Kelvin degrees) was followed. The value of  $\theta$  obtained from the present data was 105°K; previous values ranged from 90.1°K to 130°K.<sup>1-3</sup> The experimentally determined magnetic moment per Pr4+ ion was found to be 2.47. This is in good agreement with the theoretical value of 2.54  $\mu_B$ for Ce<sup>3+</sup> which is isoelectronic with Pr<sup>4+</sup>.

The question arises as to the reason for the observed difference between the present results and those of Kern. Comparison of the purity of the starting materials used and the oxygen concentrations attained in the respective specimens indicates no obvious differences. Similarly, no difference in the spectrochemical analysis for magnetic impurities were observed. At the same time the significance of the deviation between the observed cell constants (5.392 Å compared to  $5.393_7$  Å observed by Kern) could be important.

Comparison of the equilibration conditions used in the two investigations discloses some more subtle differences. As it happens, we have also investigated the phase relations of the system Pr-O at high oxygen pressure. Combined with similar studies by Sieglaff and Eyring<sup>7</sup> at lower pressures, a fairly complete picture of the P-T relations of the  $PrO_2$  phase field emerges. These relations are presented in the diagram of Fig. 2. Here it is observed that the phase boundary separating the PrO<sub>2</sub> and the PrO<sub>1.83</sub> fields is almost a straight line passing through a point at 310°C, 1 atm oxygen,<sup>8</sup> and continuing to 530°C at 2000 atm. The metastable appearance of two phases adjacent to this line results from the difficulty in achieving equilibrium at these temperatures and pressures. Also difficulty was encountered in quenching a sample so as to preserve a phase formed at high temperature and pressure. In particular, it was found that when a specimen was slowly cooled, or even when a specimen was temperature-quenched at pressure, the presence of the PrO<sub>2</sub> phase was always detected in the x-ray diffraction trace. This is in agreement with Eyring and Holmberg's comments on the rapid oxygen uptake in this system,<sup>8</sup> and results in the difficulty that a possibly disordered PrO<sub>2</sub> phase can result upon cooling from conditions at which  $PrO_{1.83}$  is stable.

In this connection, the sample measured by Kern was prepared by equilibration at 360°C and 5 atm oxygen pressure. Reference to Fig. 2 shows that the stability of PrO<sub>2</sub> under these conditions is uncertain. One questions whether the phase studied by Kern resulted from the conditions under which the sample was cooled rather than those under which it was equilibrated. The distorted structure which would be thought to result from this situation would account for the somewhat high value of the cell constant. In addition, this may very well be the reason that the crystal-field analysis attempted by Kern failed to account for the experimental data until an expanded Pr-O distance was introduced into the calculations. In turn, this distortion is thought to be the reason that antiferromagnetism was not observed by Kern in this compound.

<sup>&</sup>lt;sup>6</sup> W. Simon and L. Eyring, J. Am. Chem. Soc. **76**, 5872 (1954). <sup>6</sup> R. M. Bozorth, H. J. Williams, and D. E. Walsh, Phys. Rev. **103**, 572 (1956).

<sup>&</sup>lt;sup>7</sup>C. L. Sieglaff and L. Eyring, J. Am. Chem. Soc. **79**, 3024 (1957).

<sup>&</sup>lt;sup>8</sup> L. Eyring and B. Holmberg, in Nonstoichiometric Compounds, edited by R. Ward (American Chemical Society, Washington, D. C., 1963).