Electrical Resistivities of Single-Crystal PrTiO₃ and NdTiO₃. Magnetic Properties of PrTiO₃, NdTiO₃, PrScO₃, and NdScO₃

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Electrical resistivities were measured as a function of temperature in the range below 300 K for single-crystal samples of $PrTiO_3$ and $NdTiO_3$. Both materials are semiconductors with room temperature activation energies of 0.03 to 0.04 eV. Magnetic susceptibilities for $PrTiO_3$ and $NdTiO_3$ follow the Curie–Weiss law at high temperatures with $C_m = 1.73(3)$ and $\Theta_c = -49(3)$ K ($PrTiO_3$), and $C_m = 1.77(3)$, $\Theta_c = -35(3)$ K ($NdTiO_3$). For $PrScO_3$ and $NdScO_3$, isostructural materials, magnetic-susceptibility data also follow the Curie–Weiss law with $C_m = 1.34(3)$ and $\Theta_c = -8(2)$ K ($PrScO_3$) and $C_m = 1.51(3)$ and $\Theta_c = -32(3)$ K ($NdScO_3$). Assuming that the data for $PrScO_3$ and $NdScO_3$ represent a fair approximation to the rare-earth-only susceptibility, a Ti(III) contribution to the susceptibilities of $PrTiO_3$ and $NdTiO_3$ can be estimated and these are found to be near the spin-only value. $PrTiO_3$ shows complex magnetic order below 96(2) K, while $NdTiO_3$ shows no obvious sign of order above 4.2 K.

Introduction

The materials $RTiO_3$, R = lanthanide(III), have attracted attention recently due to the surprising variety of physical properties exhibited within an isostructural (*1*) and chemically similar series of compounds. Magnetic and electrical properties, in particular, are a strong function of R. For example, when R = La metallic resistivity (*2–4*) and a large temperature-independent paramagnetism (*2*) are observed at high temperatures. A possible metal–semiconductor transition is observed at 125 K accompanied by complex magnetic ordering phenomena (*2*). Similar behavior is observed for $CeTiO_3$ (*2*). When R = Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, or Y, the materials are all semiconductors with activation energies >0.2 eV and the

magnetic behavior is ferro (Y and Lu) (*3, 5–7*) or ferrimagnetic (Gd, Tb, Dy, Ho, Er, Tm, Yb) (*7–9*). For $YTiO_3$ the magnetic susceptibility above T_c (29 K) is of the Curie–Weiss type with a Curie constant very close to the spin-only value (*5*).

For R = La and Ce above ~100 K the magnetic and electrical properties are consistent with some form of collective electron model for the Ti(III) d electrons, although a detailed theory is not available. For R = Gd through Lu, a localized electron model seems appropriate. For the remaining compounds in the series, R = Pr, Nd, and Sm, the situation is less clear. Here we report the results of electrical and magnetic studies of $PrTiO_3$ and $NdTiO_3$ using well-characterized single-crystalline samples. The magnetic susceptibilities of the corresponding $RScO_3$ phases, R = Pr and Nd are also reported.

Experimental

Preparation and Characterization of Materials

Starting materials. Green Pr_2O_3 was prepared by hydrogen reduction of dark brown Pr_6O_{11} at 900°C for 12 hr. Ti_2O_3 was prepared by arc-melting appropriate amounts of titanium sponge (99.97%) and TiO_2 (99.95%) and adjusting the O/Ti ratio to 1.500 ± 0.005 as monitored by thermal gravimetric weight gain analysis (tga). Pr_6O_{11} and Nd_2O_3 of 99.99% purity with respect to other rare earths and 99.95% with respect to all other elements were obtained from Research Chemicals. Nd_2O_3 was fired in air at 1000°C before using.

Growth of single crystals of $PrTiO_3$ and $NdTiO_3$. Four- to five-gram charges of Pr_2O_3/Ti_2O_3 or Nd_2O_3/Ti_2O_3 were arc-melted on a molybdenum hearth of a modified Centorr Tri-Arc furnace. The crystals were pulled from the melt at a rate of 4 mm/hr. A tungsten stud, hard-soldered to a water-cooled heat pipe was used as the seeding device. Titanium-gettered argon gas was blown through the furnace during growth. Often, boules pulled by this procedure contained large single-crystal grains. The largest produced by this technique were $PrTiO_3$—180 mg and $NdTiO_3$—20 mg. Crystals of both materials were black, and precession photography of fragments displayed a $1\bar{1}0$ twin plane as described previously.

Thermal gravimetric weight-gain analysis showed that the crystals of both $PrTiO_3$ and $NdTiO_3$ were slightly oxidized. Assuming an oxygen-excess formalism (2) the actual compositions are $PrTiO_{3.012}$ and $NdTiO_{3.008}$. For $NdTiO_3$ the Nd/Ti ratio was found by neutron activation to be 0.98 ± 0.02.

Preparation and Characterization of Polycrystalline $PrScO_3$ and $NdScO_3$

$NdScO_3$ was prepared by solid-state reaction between Sc_2O_3 and Nd_2O_3 in air at 1300°C for 12 hr while $PrScO_3$ was prepared from Pr_2O_3 and Sc_2O_3 in a welded molybdenum crucible under purified argon. Sc_2O_3 (99.99%) was obtained from Research Chemicals.

These materials were characterized by X-ray powder diffractometry and $CuK\alpha$ radiation. KCl was used as an internal standard. The peak positions and relative intensities agreed well with those given in the JCPDs files 26-1353 ($PrScO_3$) and 26-1275 ($NdScO_3$). Our lattice constants, based on a *Pbnm* cell, are: $PrScO_3$ $a = 5.609(4)$, $b = 5.777(3)$, $c = 8.031(9)$ Å, and $NdScO_3$ $a = 5.586(4)$, $b = 5.772(3)$, $c = 8.017(7)$ Å.

Electrical Resistivity and Magnetic Measurements

The electrical resistivity measurements were made using the van der Pauw technique. Magnetization and susceptibility data were obtained with a PAR vibrating sample magnetometer and associated electromagnet and cryogenics. Some of the susceptibility measurements were made with a Faraday balance. Details of the measurement techniques have been presented previously (2).

Electrical resistivity data were obtained on single-crystal samples. Magnetic measurements were done on polycrystalline samples prepared by grinding small crystals from the same growth batch as the crystals used for electrical measurements.

Results and Discussion

Electrical Resistivity: $PrTiO_3$ and $NdTiO_3$

Resistivity versus temperature data for $PrTiO_3$ in the range 300 K to about 40 K are shown in Fig. 1. Clearly, $PrTiO_3$ is a semiconductor in this temperature interval. Note a change in activation energy at about 75 K. Above this temperature $E_a = 0.04$ eV and below $E_a = 0.03$ eV. This result differs significantly from that of Bazuev *et al.* (3),
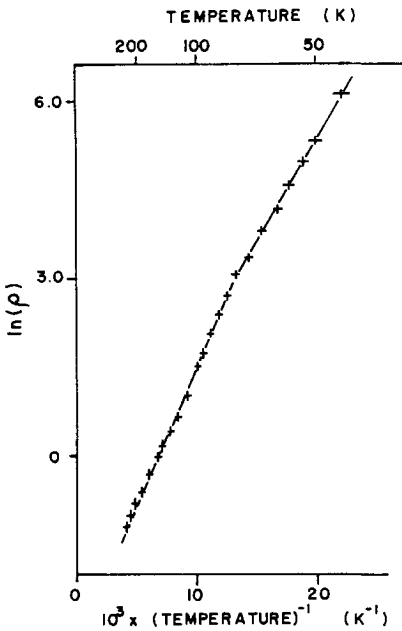
FIG. 1. Natural logarithm of the resistivity (ohm-cm) versus reciprocal temperature for $PrTiO_3$. The low-temperature ($T < 75$ K) activation energy is 0.03 eV and for $T > 75$ K it is 0.04 eV.

who report a temperature independent resistivity for a polycrystalline sample of $PrTiO_3$ in the range 300–1000 K.

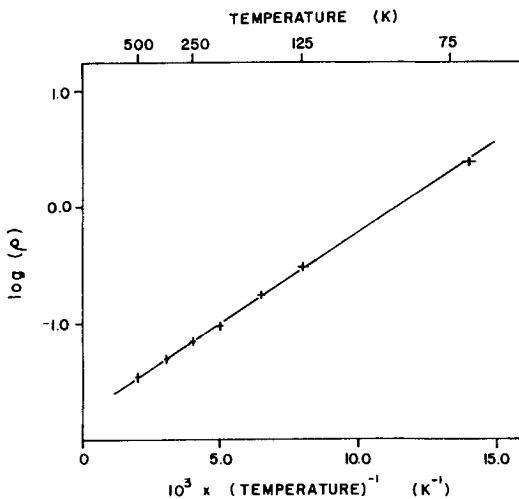Similar results are found for $NdTiO_3$ in Fig. 2. These data can be analyzed in terms

of a semiconductor model with a single activation energy, $E_a = 0.03$ eV, for the range 75–500 K. The result here is in reasonable agreement with Bazuev et al. (3) and Ganguly et al. (4), both of whom report semiconductor behavior with activation energies of 0.06 eV and 0.02 eV, respectively.

Thus, both $PrTiO_3$ and $NdTiO_3$ are semiconductors with similar activation energies. The origin of the semiconducting behavior cannot be determined from resistivity data alone. These materials could be band semiconductors such as the semiconducting form of Ti_2O_3 (10) or the conductivity could arise from the motion of small polarons, the so-called hopping model. The band semiconductor model requires collective Ti(III) d electrons while the hopping model implies localized d electrons. Magnetic data can provide information on the nature of the d electrons and these are discussed in the next section.

Magnetic Properties: $PrTiO_3$ and $NdTiO_3$

Magnetic susceptibility. The results of magnetic susceptibility measurements for $PrTiO_3$ and $NdTiO_3$ are plotted in Fig. 3. Clearly, both materials exhibit Curie–Weiss behavior over the temperature range investigated. Note that neither material
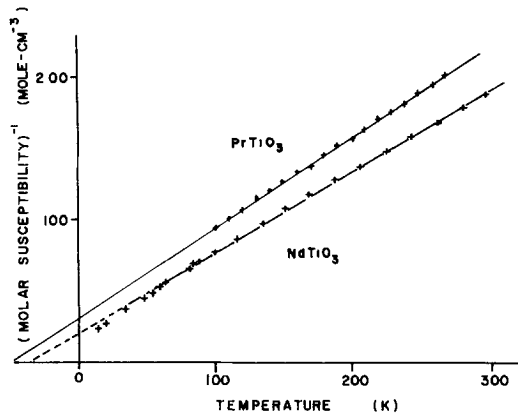

FIG. 2. Logarithm (base 10) of the resistivity (ohm-cm) versus reciprocal temperature for $NdTiO_3$.

FIG. 3. Reciprocal susceptibilities versus temperature for $PrTiO_3$ and $NdTiO_3$. The applied field for both compounds is 1.08 T.

shows a temperature-independent term as found for the metallic compounds $LaTiO_3$ and $CeTiO_3$ (2). This is strong evidence that the TIP susceptibility for these materials is entirely of the Pauli type. Curie–Weiss parameters derived by least-squares fits of the data for both compounds are shown in Table I. The problem in the interpretation of these constants is to separate the contributions of the lanthanide ions and Ti(III).

The lanthanide (III) ion contributions to the susceptibility should be closely approximated by the molar susceptibilities of the isostructural $PrScO_3$ and $NdScO_3$, where diamagnetic Sc(III) replaces Ti(III). Such data are shown in Fig. 4. Again the Curie–Weiss law holds and the constants derived from least-squares fits are also shown in Table I.

It is reasonable to conclude therefore, that in $PrTiO_3$ and $NdTiO_3$, Ti(III) makes a Curie–Weiss-type contribution to the susceptibility. This is very different from the cases of $LaTiO_3$ and $CeTiO_3$, where, as mentioned earlier, the Ti(III) contribution seems to be of the temperature-independent type. In the paramagnetic region the Curie constants are additive, so the Ti(III) contribution can be determined by the differences $C_m(PrTiO_3) - C_m(PrScO_3) = 0.39(6)$ and $C_m(NdTiO_3) - C_m(NdScO_3) =$
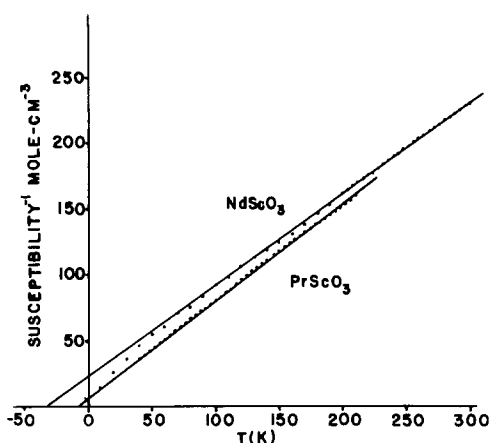

FIG. 4. Reciprocal susceptibilities versus temperature for $PrScO_3$ and $NdScO_3$. The applied fields are 1.4 T ($PrScO_3$) and 1.3 T ($NdScO_3$).

0.26(6), respectively. Both constants are near the spin-only value for Ti(III), 0.37, and that found for Ti(III) in $YTiO_3$, 0.36(5), although the errors are relatively large. We regard this as strong but circumstantial evidence that the magnetic behavior of Ti(III) in $PrTiO_3$ and $NdTiO_3$ is consistent with a localized electron model. In turn this lends support to a hopping or small-polaron model for electrical transport in these compounds.

Note that for both $PrScO_3$ and $NdScO_3$ the Curie constants are significantly smaller than the free-ion values. Similar results have been reported for a number of complex Pr and Nd oxides where the Curie–Weiss law was observed, for example $PrTiTaO_6$ ($C_m = 1.28$) (11), $NdTiTaO_6$ ($C_m = (1.36)$ (11), and $Nd_2Ti_2O_7$ ($C_m = 1.22$) (12). This can be ascribed to the influence of the crystal field.

Magnetization measurements. From the data of Fig. 5 it is clear that $PrTiO_3$ exhibits magnetic order below a critical temperature of 96 ± 2 K. The shape of the magnetization versus temperature curve is a strong function of applied field. At $H_{app} = 0.0045$ T the shape is very similar to that for $CeTiO_3$ at the same field. In addition to the critical

TABLE I

CURIE–WEISS CONSTANTS FOR $PrTiO_3$, $PrScO_3$, $NdTiO_3$, AND $NdScO_3$

Compound	$C_m{}^a$ (mole-cm^3-K^{-1})	$\Theta_c{}^a$ (K)
$PrTiO_3$	1.73(3)	−49(3)
$PrScO_3$	1.34(3)	−8(2)
Pr(III) (Free ion)	1.60	
$NdTiO_3$	1.77(3)	−35(3)
$NdScO_3$	1.51(3)	−32(3)
Nd(III)	1.62	

[a] The numbers in parentheses represent the estimated experimental uncertainty in the last significant figure. The statistical uncertainties are much smaller.
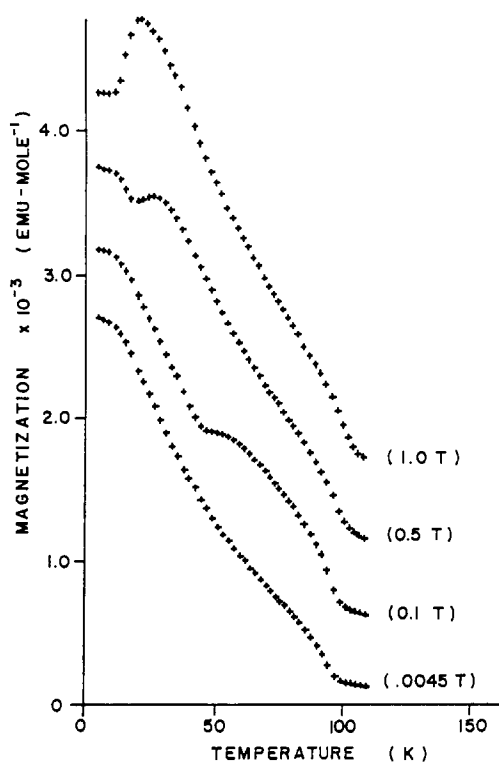
FIG. 5. Magnetization versus temperature for PrTiO₃ at various fields (indicated in brackets). With increasing field each successive curve has been displaced upward by 0.5×10^{-3} emu mole^{-1} for clarity.

FIG. 6. Magnetization versus applied field at 4.2 K for PrTiO₃. The curve shown is for decreasing field.

temperature at 96 K there is an inflection at lower temperatures, about 50 K. In view of the fact that LaTiO₃ orders at 125 K it is tempting to assume that the Ti(III) sublattice orders at 96 K, while the 50-K inflection signals order in the Pr(III) sublattice. If this is true, then the values of the Ti(III) moment are much greater than those found in LaTiO₃. For example, at 82 K the moment for PrTiO₃ is about 1.10 μ_B/F.U. while at 4.2 K the moment for LaTiO₃ is only 0.007 μ_B/F.U.

As the applied field is increased an additional "hump" appears in the magnetization–temperature curve, the center of which moves to lower temperatures with increasing field. The isothermal magnetization–field curve at 4.2 K also has an interesting shape for decreasing field, Fig. 6. For
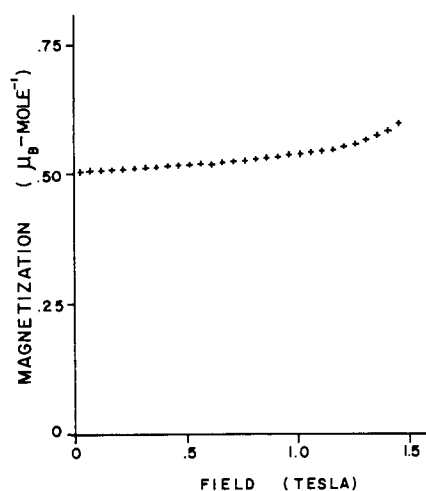
fields up to about 0.8 T saturation behavior is found at a value of 0.50 μ_B/F.U. while for higher fields the moment begins to increase rapidly.

As far as they go, the results of Bazuev *et al.* (*13*) are in agreement with these results. They report $T_c = 90$ K for PrTiO₃ but did not carry their magnetization measurements to 4.2 K. Their interpretation of the magnetic properties in terms of a canted antiferromagnetic model seems suspect in view of the high moment at 4.2 K observed here, 0.50 μ_B/F.U. Canted AF order in the isostructural RFeO₃ series, where Fe(III) has a much greater moment than Ti(III) gives rise to low-temperature moments of only 0.05 μ_B/F.U. (*14, 15*). An investigation of the magnetic structure of this complex material using neutron diffraction techniques is currently under way.

In contrast, NdTiO₃, as one can see from Fig. 3, shows no obvious sign of magnetic order down to 4.2 K. This is further illustrated by the data of Fig. 7. Here we compare isothermal (4.2 K) magnetization field data with that calculated for a $J = \frac{1}{2}$ paramagnet (Nd(III), 4f^3, and Ti(III) are Kramer's ions). A good fit is obtained for an average effective g value of 2.32. The Bril-
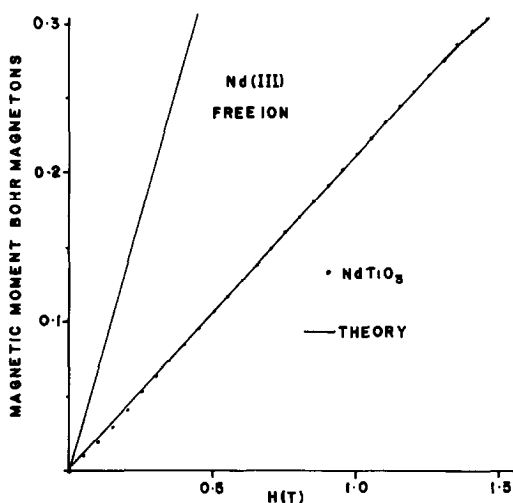
FIG. 7. Magnetization versus applied field for Nd-TiO$_3$. The solid line is a Brillouin function, $J = \frac{1}{2}$, $\langle g \rangle$ = 2.32. Also shown is the free-ion Brillouin function for Nd^{3+}, $J = \frac{9}{2}$, $g = 8/11$.

louin function for the Nd^{3+} free ion, $J = \frac{9}{2}$, g = 8/11, is shown for comparison. This is evidence for a strong quenching of the Nd^{3+} paramagnetism by the crystal field at low temperature. Note also from Table I, that the Weiss constants, Θ_c, of NdTiO$_3$ and NdScO$_3$ are identical to within experimental error. This suggests that the negative Θ_c for NdTiO$_3$ has its origin in crystal field effects rather than in exchange. The Θ_c values for PrTiO$_3$, in which exchange is important, and PrScO$_3$, a paramagnet, differ substantially. Although the circumstantial evidence for absence of magnetic order in NdTiO$_3$ is strong, the question cannot be settled without appeal to a definitive technique such as neutron scattering. From a more limited set of data both Ganguly et al. (4) and Bazuev et al. (13) draw similar conclusions regarding NdTiO$_3$.

If it is true that NdTiO$_3$ is paramagnetic to 4.2 K, this is a most extraordinary situation as shown by the contents of Table II. Here we list the observed critical temperatures for all of the RTiO$_3$ phases for which data are available.

TABLE II

CRITICAL TEMPERATURES FOR THE RTiO$_3$ COMPOUNDS

R	$T_c{}^a$ (K)	R	$T_c{}^a$ (K)
La	125	Gd	34
Ce	116	Tb	49
Pr	96	Dy	64
Nd	<4.2	Ho	56
Sm	?	Er	41
Eu^b	—	Tm	58
		Yb	39

^{a} Data are taken from Refs. (2, 7, 9).

^{b} EuTiO$_3$ contains Eu(II) and Ti(IV) and is therefore not properly a member of this series.

From this comparison, NdTiO$_3$ is the only RTiO$_3$ phase without a T_c substantially greater than 4.2 K. Furthermore, the neighboring member of the series, PrTiO$_3$, has T_c = 96 K. An explanation is not available at the present time. Information about SmTiO$_3$ would also be desirable.

In conclusion, both PrTiO$_3$ and NdTiO$_3$ are semiconductors with relatively small activation energies ~0.03 to 0.04 eV. In the case of PrTiO$_3$ this is a significantly different result from previous reports (3). By comparing the paramagnetic susceptibilities of PrTiO$_3$ and NdTiO$_3$ with the isostructural PrScO$_3$ and NdScO$_3$ it is concluded that Ti(III) contributes a term which is essentially that expected for a spin-only, d^1 ion. These two facts indicate that the d electrons in PrTiO$_3$ and NdTiO$_3$ are localized at Ti(III) sites. It was further noted that PrTiO$_3$ orders magnetically below 96 K, while NdTiO$_3$ shows no obvious signs of order above 4.2 K. This rather surprising fact was put into context by comparing the known critical temperatures of the remaining RTiO$_3$ phases. To compare these results with those obtained for LaTiO$_3$ and CeTiO$_3$ we note that a metal–semiconductor transition occurs as a function of the rare earth element between R = Ce and R = Pr.

Acknowledgments

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