Inorg. Chem. **1981**, *20*, 1025–1029 **1025**

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Crystal Growth, Electrical Resistivity, and Magnetic Properties of $LaTiO_3$ and $CeTiO_3$. Evidence for a Metal–Semiconductor Transition

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Received July 7, 1980

Crystals were grown from the melt with use of Bridgman-Stockbarger and Czochralski techniques. Analysis indicated slightly oxidized products, the composition of which can be expressed as $LaTiO_{3.011}$ and $CeTiO_{3.013}$. Both materials show metallic resistivity behavior from 300 to 125 K ($LaTiO_3$) or 60 K ($CeTiO_3$). Below these temperatures, the resistivity data can be fitted to a semiconductor model with activation energies of 0.01 ($LaTiO_3$) and 0.001 eV ($CeTiO_3$). From 300 to 125 K the susceptibility of $LaTiO_3$ is temperature independent, while below this temperature evidence for weak ferromagnetism, $\mu_{SAT} = 7 \times 10^{-3}\ \mu_B$ (4.2 K), is found. $CeTiO_3$ orders magnetically below 116 K. There is a second anomaly in the magnetization near 60 K. Above 116 K, susceptibility data can be fitted to a Curie–Weiss plus a TIP term yielding $C_m = 0.55$, $\Theta_c = -5$, and $\chi_{TIP} = 860 \times 10^{-6}$ cm^3 mol^{-1}. These properties are discussed in terms of highly speculative models for the electronic structure.

Introduction

It has been suggested that the series of compounds $RTiO_3$, where R = lanthanide(III), presents an opportunity to study the transition from collective to localized behavior for the d electrons on the Ti(III) ions.[1] This suggestion was based largely upon unpublished reports that $LaTiO_3$ is metallic and Pauli paramagnetic, while $GdTiO_3$ is semiconducting and ferromagnetic at low temperatures. Subsequent studies, carried out on polycrystalline specimens, for which characterization details were not always reported, tend to support this position.[2-4]

Recently, we reported detailed structural data, obtained from single-crystal X-ray diffraction studies, for selected members of the $RTiO_3$ series.[5] These data established the $GdFeO_3$ structure type for R = La, Nd, Sm, Gd, and Y and by reasonable extension, all members of the series. In addition a quantitative measure of the structural parameters important to the collective to localized electron transition was obtained. For example, Goodenough has proposed that the Ti–O–Ti bond angle is a crucial parameter in these materials.[1] There are no short Ti–Ti contacts, so the d–d interaction occurs through an intervening oxide ion. The interaction parameter is the transfer integral, b_π, as the d electron occupies a molecular orbital of π symmetry. It is taken as axiomatic that the transfer integral will diminish as the Ti–O–Ti bond angle decreases from 180°. For the $RTiO_3$ series, the mean bond angle varies from 157 (R = La) to 142° (R = Y).[5] Thus, the magnitude of b (dropping the subscript) is controlled by the size of the R species and should decrease as R decreases from La(III) (1.32 Å) to Y(III) 1.15 Å).[6]

Goodenough has attempted to relate the magnitude of b to various observables such as transport properties, magnetic ordering temperatures, and types of magnetic order by means of the phase diagram shown in Figure 1. Changes in transport and magnetic properties are expected as b decreases from right to left, and profound changes occur at critical values of b. For $b > b_m$, the electrons are collective, correlations are weak, and metallic conductivity and Pauli paramagnetism are anticipated. For $b_c < b < b_m$, the electrons are still collective, but correlation is strong and semiconducting properties should be observed along with a variety of magnetic phenomena including antiferromagnetic and ferromagnetic spiral structures (AFS and FS) and normal ferromagnetism. For $b < b_c$, a localized electron picture should hold, and ferromagnetism is predicted at low temperatures.

We have investigated some physical properties of selected members of the $RTiO_3$ series using reasonably well-characterized crystalline samples and have extended the measurements to lower temperatures than reported previously. The results of magnetic susceptibility and electrical resistivity measurements on $LaTiO_3$ and $CeTiO_3$ are discussed here, and comparisons are made to previous work. A preliminary report of some of this work was presented elsewhere.[7] The relevance of Figure 1 for these compounds is considered. We have also reported elsewhere magnetic susceptibility data for the compounds R = Gd, Tb, Dy, Ho, Er, and Tm[8] and neutron diffraction data for R = Er and Ho.[9] The remaining compounds in the series will be the subject of future publications.

Experimental Section

Preparation and Characterization of Materials. $LaTiO_3$. Crystals of $LaTiO_3$ which were largely single except for the presence of twin components as described previously[5] were grown from the melt. About 8 g of $LaTiO_3$ were melted (mp 2080 ± 50 °C) in an open molybdenum crucible of 2.5-cm diameter. The crystal growth was carried out in an ADL model MP crystal-growth furnace with use of RF heating under an atmosphere of purified argon. The charge was cooled at about 50 °C/h for 12 h and then quenched. The crystals grew as slabs 2–5 mm on an edge and about 0.5 mm thick with the thin dimension perpendicular to the crucible axis. These crystals are from the same batch as those used for the structure determination.[5] Thermogravimetric weight-gain analysis (TGA) showed that the crystals were slightly oxidized. By expression of this as an oxygen excess, i.e., on the assumption that La/Ti = 1.00, the composition would be $LaTiO_{3.011}$. Alternatively, the oxidation could result from a slight La deficiency as this would require conversion of some Ti(III) to Ti(IV) for charge compensation. The composition on the assumption that Ti/O = 3.00 would be $La_{0.992}TiO_3$. The slightly low value of the experimental density, 6.25 g cm^{-3}, compared with the theoretical density, 6.30 g cm^{-3}, argues for the cation deficiency model. This type of nonstoichiometry has been found in a number of oxidized rare-earth transition-metal perovskites.[10]

$CeTiO_3$. Polycrystalline $CeTiO_3$ was prepared by reacting CeO_2 with TiO at 1400 °C for 12 h in a welded molybdenum crucible filled with ~200 torr of high-purity argon. TiO was prepared by arc melting Ti metal (99.97%) and TiO_2 (99.95%). By TGA of the product the Ti/O ratio was controlled to 1.000 ± 0.005. Crystal growth was done by the Czochralski technique using a modified Centorr Tri-Arc furnace with a molybdenum hearth. A tungsten seed rod was silver-soldered

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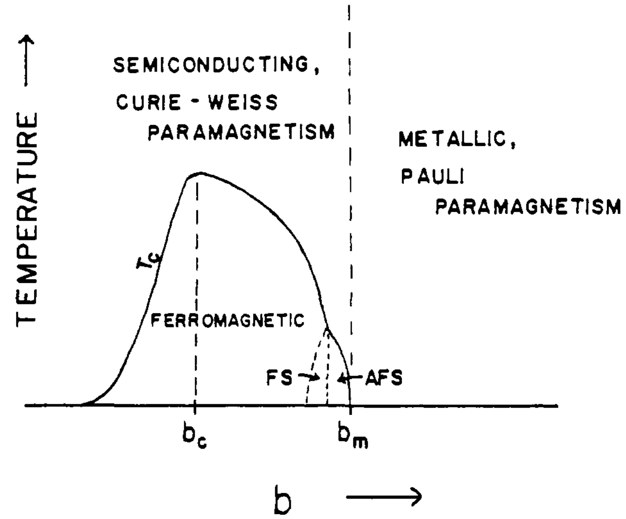

Figure 1. Qualitative phase diagram showing the dependence of electrical and magnetic properties on the magnitude of the transfer integral, *b* (adapted from ref 1).

to a heat pipe and attached to a pulling head. Pulling rates of 4 mm/h were used, and under favorable conditions pyramidal crystals of a few millimeters on a side, weighing about 0.020 g, were obtained. An atmosphere of Ti-gettered argon was blown through the furnace during growth. Precession photographs of small crystals from the growth batch showed that the as-grown $CeTiO_3$ crystals contained the same type of twin components as found in $LaTiO_3$.[5] Weight-gain analysis (TGA) indicated that the composition of the crystals was $CeTiO_{3.013}$ or $Ce_{0.991}TiO_3$.

General Remarks. The rare-earth oxides used in all preparations were obtained from Research Chemicals with stated purity 99.99% with respect to other rare earths and 99.95% with respect to other elements. Emission spectrographic analysis of the starting materials and the as-grown crystals showed no impurities, including molybdenum, at levels greater than 100 ppm. The crystals were black and there was no metallic luster.

Electrical Resistivity Measurements. These were obtained using the van der Pauw technique[11] over the temperature range from 300 to 4.2 K. The samples consisted of disks cut from the crystals of about 0.20 mm thickness. Electrical contacts were made with evaporated indium. Crystals were mounted on IC headers with low-temperature varnish, and silver paste was used to connect the indium contacts and four header pins. A chromel—gold–0.07% iron thermocouple was mounted near the crystal.

Magnetization and Magnetic Susceptibility Measurements. Magnetization data were obtained using a Princeton Applied Research vibrating-sample magnetometer and a Magnion electromagnet. The magnetometer was calibrated with a nickel sphere with use of the accepted value of 58.6 ± 0.1 emu g^{-1} at 4.2 K for the magnetic moment of nickel.[12] Temperature was monitored with use of a calibrated chromel—gold–0.07% iron thermocouple.

Susceptibility data in the temperature range 80 to 300 K were obtained via the Faraday technique through the courtesy of Professor A. P. B. Lever at York University.

Results and Discussion

$LaTiO_3$. Figure 2 shows the results of electrical resistivity and magnetic susceptibility measurements on crystals of $LaTiO_3$. The susceptibility data are from a polycrystalline sample obtained by grinding the crystals. Two sets of resistivity data are shown. One set was obtained by using a conventional four-probe geometry courtesy of Dr. R. D. Shannon and J. L. Gillson of Du Pont, Wilmington, DE. Crystals used in both experiments were from the same growth batch. These are also from the same batch as crystals used in the structure determination.[5] The agreement is satisfactory, the differences probably being due to uncertainties in geometrical factors. From 300 to 125 K, the resistivity decreases. This behavior is characteristic of metals and is consistent with a model involving collective electrons moving in a partially filled band. Note the value of the resistivity at 300 K of 10^{-2} Ω cm. This is unusually high for metals and may indicate that the bands involved are very narrow or even overlapping as in semimetals. Bazuev et al.[4] reported resistivity data on polycrystalline samples of $LaTiO_3$ from 300 to 1000 K, finding metallic behavior and a similar room-temperature resistivity. Ganguly et al.,[2] again with polycrystalline samples, also report metallic resistivity from 300 to 150 K.

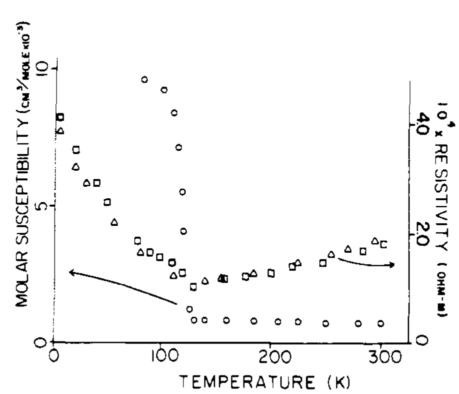

Figure 2. Electrical resistivity and magnetic susceptibility vs. temperature for $LaTiO_3$ crystals: △, this work; □, Shannon and Gillson.

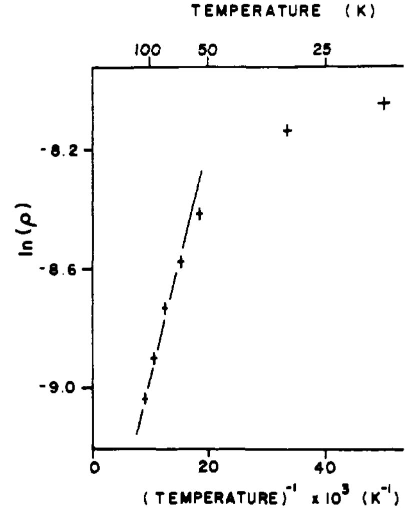

Figure 3. Semiconducting behavior of $LaTiO_3$ below 125 K. The activation energy is 0.01 eV.

The temperature-independent paramagnetic susceptibility between 300 and 125 K can be interpreted as Pauli paramagnetism and therefore supports the collective electron model. This susceptibility is quite large $\chi_m = (800 \pm 30) \times 10^{-6}$ cm^3 mol^{-1}, indicative of a high density of states at the Fermi level with possible exchange enhancement as well. Both effects are consistent with a narrow conduction band model. Our susceptibility data are in good agreement with those of Bazuev et al.,[4] who also report temperature-independent susceptibility over the same range with a value of 600 × 10^{-6} cm^3 mol^{-1}, but are in conflict with those of Ganguly et al.,[2] who found a temperature-dependent susceptibility in this range.

Below 125 K, there occur pronounced changes in both the resistivity and susceptibility. Note the distinct minimum in the resistivity at 125 K followed by an increase with decreasing temperature such that the value at 4.2 K is actually about twice that at 300 K. Figure 3 shows the data below 125 K plotted as log ρ vs. T^{-1}. There is a linear portion to 50 K from which an activation energy of 0.01 eV can be extracted. The data

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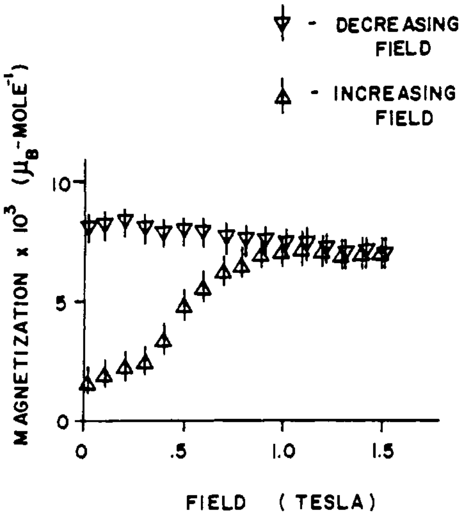

Figure 4. Magnetization of $LaTiO_3$ at 4.2 K.

below 50 K cannot be fitted with the same activation energy. The behavior of $LaTiO_3$ below 125 K is characteristic of a semiconductor, indicating an apparent metal to semiconductor transition at about 125 K. We are the first to report this effect in $LaTiO_3$.

Accompanying the metal–semiconductor transition at 125 K is a dramatic increase in the magnetic susceptibility. The shape of the susceptibility–temperature curve to 77 K (Figure 2) suggests a ferromagnetic state below 125 K. The behavior of the magnetization vs. field curve (4.2 K) (Figure 4) shows an S shape with increasing field, pronounced hysteresis, and a small saturation amount of 7×10^{-3} μ_B mol^{-1}. Such evidence suggests a more complex magnetic structure. Our results below 125 K are in reasonable agreement with those of Bazuev et al.,[4] but we have extended the measurements to 4.2 K, disclosing the unusual low-temperature magnetization curve and providing a value for the saturation moment.

At this stage, a number of interpretations of the $LaTiO_3$ behavior are possible. For example, the resistivity data alone are consistent with a narrow-gap semiconductor model. Degenerate behavior is expected for semiconductors with band gaps which are on the order of thermal energies $E_{gap} \lesssim 10^{-2}$ eV. For $kT > E_{gap}$, the Fermi level lies above the bottom of the conduction band, and metallic-like behavior is observed. As kT decreases, the Fermi level drops below the conduction band minimum, and semiconducting behavior can be observed. If we interpret the activation energy observed below 125 K as $E_{gap}/2$, then E_{gap} for $LaTiO_3$ is 0.02 eV. It is worth noting that the resistivity data for $LaTiO_3$ are very similar to those for the alloy 12% Sb in Bi, a degenerate semiconductor with a band gap of 0.02 eV.[13]

A band semiconductor model for $LaTiO_3$ represents a departure from the usual treatment of these perovskite oxides as first proposed by Goodenough.[1] Goodenough argues that at points of high symmetry in the Brillouin zone, e.g., $k = 0$, the band structure of these materials should resemble that expected for the cubic perovskites, *Pm3m*, with 1 formula unit per cell. As there is only one d electron per Ti(III), no conduction band can be more than $^1/_2$ filled, and a metallic state must result in the weak correlation, collective electron limit. For the $GdFeO_3$ structure type, there are four Ti(III) per cell, i.e., an even number of d electrons, and a semiconductor is not impossible. Clearly, band structure calculations on $LaTiO_3$ would be valuable.

So, on the small gap semiconductor model, there is no fundamental change in electronic structure for $LaTiO_3$ as a function of temperature. The onset of the magnetic anomaly at about the same temperature as the change in electrical properties must then be regarded as coincidental. The magnetic anomaly below 125 K might be ascribed to a ferromagnetic impurity. However, no impurities could be detected above 100 ppm in $LaTiO_3$. The most likely impurities would be the heavy rare-earth $RTiO_3$ phases, R = Gd to Lu, but none of these materials have critical temperatures above 60 K.[7]

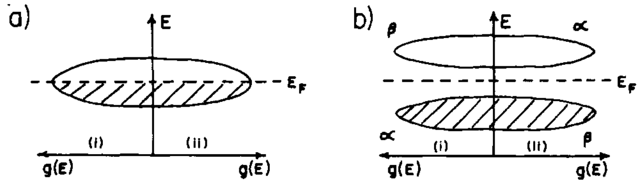

Figure 5. Schematic density of states diagrams showing the coincidence of the metal–semiconductor transition and the paramagnetic to itinerant antiferromagnetic transition in $LaTiO_3$: (a) $T > T_c$; (b) $T < T_c$.

Another possible model is analogous to that proposed for $SrVO_3$, an isoelectronic material containing V(IV), which has the ideal, cubic perovskite structure.[14] The magnetic and electrical properties of $SrVO_3$ resemble those of $LaTiO_3$ in some respects. Both show metallic conductivity over the temperature range 300 to about 100 K, and both show a transition to a weak ferromagnetic state, $T_c = 85$ K for $SrVO_3$, at low temperatures. In fact, the spontaneous moment at 4.2 K is identical, 7×10^{-3} μ_B, for both materials. Unfortunately, resistivity data have not been reported below T_c for $SrVO_3$. The susceptibility above T_c is not of the Curie–Weiss type but is not temperature independent either. The low-temperature magnetic properties of $SrVO_3$ have been explained in terms of a ferromagnetic spin-density wave.[14] Although the low-temperature magnetic properties of $LaTiO_3$ might be explained on a similar model, the semiconducting behavior below T_c cannot be understood.[15] Thus, in spite of obvious similarities, it is not clear that the ferromagnetic spin density wave model proposed for $SrVO_3$ can be easily adapted to the case of $LaTiO_3$.

One model which is consistent with both the resistivity and the magnetic data is outlined with the aid of Figure 5. Above the transition temperature (Figure 5a), $LaTiO_3$ is metallic, implying a partially filled band, and we envisage a half-filled, narrow band. The density of states curve is artificially divided between two sublattices i and ii. Below 125 K, antiferromagnetic order sets in. The sublattices will be subjected to an exchange field which is opposite in sign for sublattices i and ii, and each band is split into α and β spin subbands as in Figure 5b. Because the unsplit band was half-filled, the low-lying α or β spin subband will be filled, the higher lying band will be empty, and the result is a semiconductor with a band gap on the order of the exchange interaction, kT_c. The low-moment ferromagnetic behavior can be understood if there is a canting between the moments on sublattices i and ii. Canted AF order is symmetry allowed and is commonly found in materials with the $GdFeO_3$, *Pbnm*, structure type.[16] A similar explanation was proposed to explain the magnetic properties of the itinerant antiferromagnet $CaCrO_3$.[17]

On this model, then, there is a true metal–semiconductor transition in $LaTiO_3$ associated with the onset of antiferromagnetic order. It should be noted that this type of metal–

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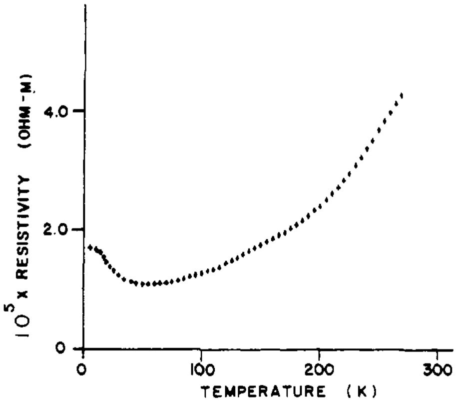

Figure 6. Temperature dependence of the resistivity of $CeTiO_3$.

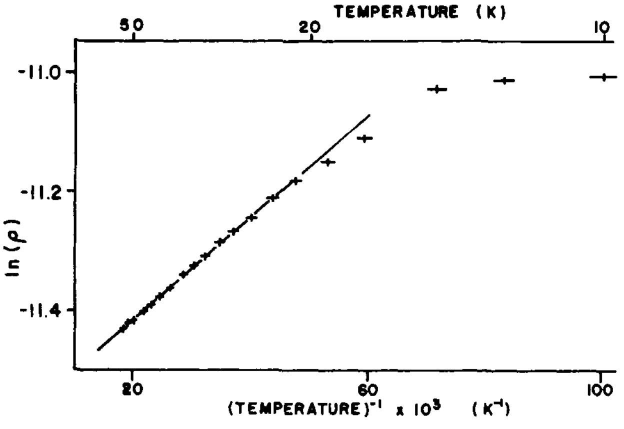

Figure 7. Semiconducting behavior of $CeTiO_3$ below 60 K. The activation energy is 0.001 eV.

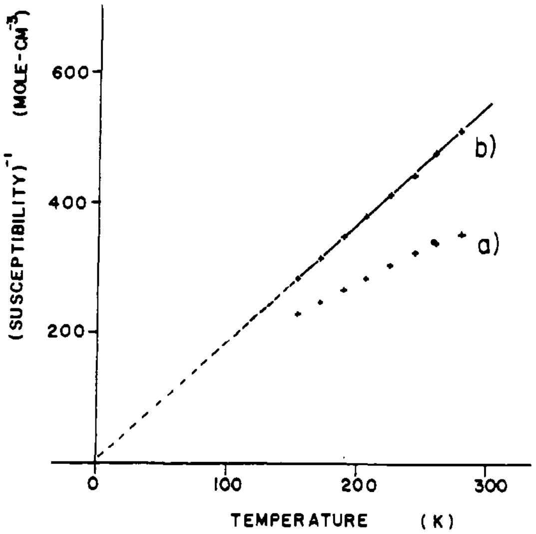

Figure 8. Inverse magnetic susceptibility vs. temperature for $CeTiO_3$ from 300 to 100 K. Curve a represents the raw data; in curve b the data are analyzed as $\chi - \chi_{TIP} = C_m/(T - \Theta)$.

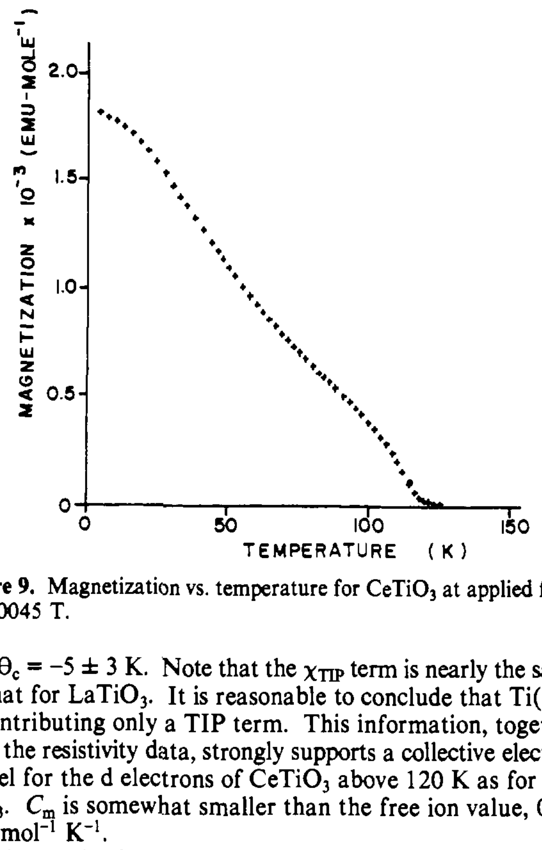

Figure 9. Magnetization vs. temperature for $CeTiO_3$ at applied field of 0.0045 T.

semiconductor transition was first proposed by Slater[18] in connection with other transition-metal oxides.

Other models may be possible as well. Further experimental and theoretical studies will be necessary to clarify the situation with $LaTiO_3$. Polarized neutron diffraction studies would be valuable in elucidating the magnetic structure of this unusual material.

$CeTiO_3$. In many respects, the behavior of $CeTiO_3$ is similar to that for $LaTiO_3$. Figure 6 shows the behavior of the resisitivity as a function of temperature. First, note that from 300 to about 90 K the temperature dependence is metallic. Surprisingly, the room-temperature resistivity of $CeTiO_3$ is an order of magnitude lower than for $LaTiO_3$. These results are in sharp contrast to those of Bazuev et al.,[19] who report a temperature-independent resistivity for polycrystalline $CeTiO_3$. Below 60 K, the resistivity increases with decreasing temperature. This part of the data can be fitted with reasonable success to a semiconductor model with an activation energy of 0.001 eV as shown in Figure 7.

One expects that the magnetic properties of $CeTiO_3$ will be determined by contributions from both Ce(III) and Ti(III). Susceptibility data in the range 300 to 120 K are shown in Figure 8. The curvature of the χ^{-1} vs. T plot (Figure 8a) suggests contributions from both temperature-dependent and temperature-independent terms. This data can be fitted to $\chi = C/(T - \Theta) + \chi_{TIP}$ and the result, plotted as $\chi^{-1}_{corr} = (\chi_{obsd} - \chi_{TIP})^{-1} = C_m/(T - \Theta)$ is shown in (Figure 8b). The correlation coefficient is 0.999 94, and the derived parameters are $C_m = 0.55 \pm 0.03$ cm^3 K^{-1} mol^{-1}, $\chi_{TIP} = 860 \pm 10$ cm^3 mol^{-1}, and $\Theta_c = -5 \pm 3$ K. Note that the χ_{TIP} term is nearly the same as that for $LaTiO_3$. It is reasonable to conclude that Ti(III) is contributing only a TIP term. This information, together with the resistivity data, strongly supports a collective electron model for the d electrons of $CeTiO_3$ above 120 K as for $LaTiO_3$. C_m is somewhat smaller than the free ion value, 0.80 cm^3 mol^{-1} K^{-1}.

This may be due to crystal field effects. For example, the material $CeTa_3O_9$ contains Ce(III) as the only paramagnetic species and has a perovskite-related structure. The susceptibility from 300 to 100 K follows the Curie–Weiss law with $C_m = 0.65$ cm^3 K^{-1}.[19] It is reasonable to conclude that only Ce(III) contributes to the Curie–Weiss term. Our susceptibility results differ sharply from those of Bazuev et al.,[4] who report only Curie–Weiss behavior (no TIP term), $C = 1.02$ cm^3 mol^{-1} K^{-1}, and $\Theta_c = -72$ K.

Magnetization–temperature data obtained at the low field of 0.0045 T (Figure 9) show evidence of magnetic order in $CeTiO_3$ below 116 ± 2 K. Note that, in addition to the critical temperature, there is another inflection or anomaly between 50 and 60 K. Unlike the case of $LaTiO_3$, the minimum in the resistivity does not coincide with the critical temperature. The

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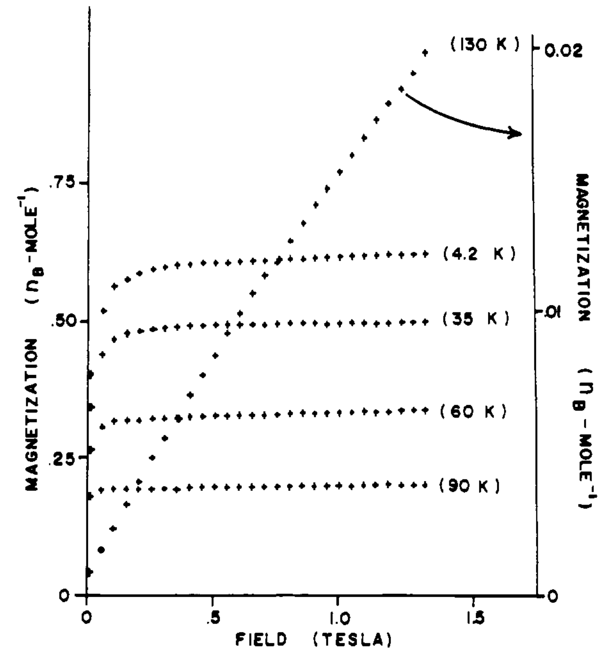

Figure 10. Magnetization vs. field for CeTiO$_3$ at various temperatures.

onset of semiconducting behavior at about 60 K does correspond to the low-temperature magnetic anomaly.

The magnetization vs. field behavior for CeTiO$_3$ at various temperatures is shown in Figure 10. All curves for $T < T_c$ saturate at very low applied fields, suggesting a ferro- or ferrimagnetic structure. The magnetization values, even for T close to T_c, are greater by at least an order of magnitude than for LaTiO$_3$. At 4.2 K, the saturation moment is 0.60 ± 0.01 μ_B, 10^2 greater than LaTiO$_3$.

Our results on CeTiO$_3$ for $T < T_c$ compare fairly well with those of Bazuev et al.[20] within the range of their measurements (300–60 K). They report a T_c of 124 K to our 116 ± 2 K and a saturation moment at 60 K of 0.22 μ_B while we measure 0.30 μ_B. Their interpretation of the CeTiO$_3$ behavior invokes a canted antiferromagnetic ordering of local moments on the Ti(III) sites in analogy with the semiconducting RVO$_3$, RCrO$_3$, and RFeO$_3$ phases. This is formally similar to one of the possible models for LaTiO$_3$, the canted moment, itinerant electron, antiferromagnetic model. Given the very weak Ti(III) moments measured in LaTiO$_3$, those observed in CeTiO$_3$ seem much too large to be understood in terms of a Ti(III) contribution only. The nature of magnetic ordering in CeTiO$_3$ and the manner in which the Ce(III) moments are involved cannot be determined from the existing data. The critical temperature at 116 K might be due to ordering of Ce(III) moments by an indirect exchange mechanism involving itinerant Ti(III) d electrons, and the 60 K anomaly could be due to the onset of spontaneous magnetism in the Ti(III) band consistent with the onset of semiconducting behavior. The saturation moment of 0.60 μ_B is difficult to understand on a simple ferro- or ferrimagnetic model. The free ion Ce(III) moment is 2.1 μ_B, although one might expect some reduction due to the crystal field interaction, while the Ti(III) moment cannot be greater than 1.0 μ_B. Again, polarized neutron diffraction experiments would aid greatly in the characterization of this unusual material.

Summary and Conclusions

Both LaTiO$_3$ and CeTiO$_3$ exhibit metallic resistivity and Pauli paramagnetism between 300 and about 100 K. These facts are consistent with collective Ti(III) d electrons in a partially filled narrow band. In terms of Figure 1, this implies that $b \gtrsim b_m$. In both compounds, magnetic order occurs below 125 (LaTiO$_3$) and 116 K (CeTiO$_3$). For LaTiO$_3$, the onset of magnetic order is accompanied by an apparent metal–semiconductor transition. A metal–semiconductor transition also occurs in CeTiO$_3$ around 60 K which coincides with a second magnetic anomaly. Probably, the electrons remain collective in the semiconducting state. This suggests that b decreases with temperature for these materials with $b > b_m$ above T_c and $b < b_m$ below T_c. The nature of the magnetic order in either compound appears to be some form of weak ferro- or ferrimagnetism, but this cannot be determined with the present data. A number of speculative models for the behavior of the two materials are presented.

Acknowledgment. We wish to thank the NSERC of Canada for financial support. D.A.M. held a 1967 Science Scholarship from 1975 to 1979. Professors R. W. Datars and C. V. Stager made available laboratory equipment and contributed useful suggestions. Mr. E. Batalla assisted with the resistivity measurements. Dr. R. D. Shannon and J. Gillson obtained a second set of resistivity data for LaTiO$_3$. Magnetic susceptibility data were obtained with use of a Faraday balance through the courtesy of Professor A. P. B. Lever of York University.

Registry No. LaTiO$_3$, 12201-04-6; CeTiO$_3$, 12185-87-4.

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