

Electrical and magnetic properties of the two crystallographic forms of BaRuO₃

J. T. Rijssenbeek

Department of Chemistry and Materials Institute, Princeton University, Princeton, New Jersey 08544

R. Jin, Yu. Zadorozhny, and Y. Liu

Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802

B. Batlogg

Lucent Technologies Bell Laboratories, Murray Hill, New Jersey 07974

R. J. Cava

Department of Chemistry and Materials Institute, Princeton University, Princeton, New Jersey 08544

(Received 13 April 1998)

We report the results of magnetic susceptibility and electrical resistivity measurements on single crystals of the nine-layer and four-layer crystallographic forms of BaRuO₃. The two forms differ in the relative amounts of corner and face sharing of RuO₆ octahedra. They display qualitatively different properties below approximately 100 K: the four-layer form shows a metallic resistivity down to low temperatures, while the nine-layer shows a crossover to a more resistive state. No local moment magnetism is observed in either phase below 400 K, which is of particular interest in the context of previously observed magnetic and superconducting phases in the Sr-Ru-O system. Resistive measurements to temperatures below 0.1 K reveal no occurrence of superconductivity in either form. [S0163-1829(99)09307-8]

Introduction. The exotic electronic state that leads to superconductivity at high temperatures in the layered copper oxides has stimulated research into the physical properties of a wide variety of unusual transition-metal oxides. Among those of recent interest, the simple ruthenates have been the subject of considerable study, especially since the discovery of superconductivity near 1 K in the layered compound Sr₂RuO₄. Experiments on that compound have indicated that the electronic state is not conventional.^{1,2} In particular, the lack of a local moment for the formally Ru⁴⁺ *S*=1 ion in this layered compound is intriguing. Sr₂RuO₄ belongs to the Ruddlesden-Popper series, Sr_{*n*+1}Ru_{*n*}O_{3*n*+1} (*n*=1, 2, 3, and infinity). The three-dimensional compound SrRuO₃ is a ferromagnetic, nonsuperconducting metal with a saturated local moment of 0.85 μ_B and the intermediate dimensionality compound Sr₃Ru₂O₇ has local moments but shows no long-range magnetic ordering³⁻⁷ even though RuO₆ octahedra are the central building blocks of all three compounds. Electrical measurements carried out on SrRuO₃ (down to approximately 4 K) and Sr₃Ru₂O₇ (down to 0.3 K) have shown that neither of them is a superconductor, although both show metallic behavior down to the lowest temperatures measured. Therefore, it appears from the materials thus far characterized that the suppression of the local moment gives way to superconductivity. However, whether there is a link between the lack of local moment and the strongly anisotropic, nearly two-dimensional nature of the system in Sr₂RuO₄ is not clear. Furthermore, whether the variation in the electrical and magnetic properties in the Sr_{*n*+1}Ru_{*n*}O_{3*n*+1} system is dictated mainly by the chemical composition or the crystalline structure has not been addressed.

In order to gain physical and chemical insight into these issues, we have carried out studies on single crystals of hexagonal BaRuO₃. Although chemically related to the stron-

tium ruthenates, BaRuO₃ displays crystal structures based on a distinctly different structure type, for which there are no analogs in the Sr-Ru-O or Ca-Ru-O systems. BaRuO₃ has three crystallographic forms, representatives of the "hexagonal Perovskite" family. These different forms, known as the nine-layer, six-layer, and four-layer compounds, have different amounts of corner and face sharing of the component RuO₆ octahedra, which in turn results in different relative contributions of Ru-Ru and Ru-O-Ru interactions to the electronic structure. Here, we report the electrical and magnetic properties of single crystals of two forms of BaRuO₃, one of which, the four-layer form, has only rarely been synthesized, showing that the properties differ considerably in the different crystallographic forms even though the chemical composition is identical. The results indicate that there may be parallels between the electronic state of these phases and that of the superconductor Sr₂RuO₄.

The crystal structures of the two forms of BaRuO₃ studied here are shown schematically in Fig. 1.⁸⁻⁹ The more commonly found nine-layer (9L) crystallographic form consists of units of three RuO₆ octahedra sharing faces in a partial chain, facilitating direct Ru-Ru *d* orbital interactions within the group, with each of these triple units of octahedra connected to its neighbors along the hexagonal axis by perovskitelike corner sharing with the nearly 180° Ru-O-Ru bonds favorable for superexchange coupling. The stacking pattern repeats after nine octahedra. Similarly, the less-common four-layer (4L) crystallographic form consists of units of two octahedra sharing faces connected to each other by perovskite-type corner sharing, with a repeating stacking pattern along the hexagonal axis after four octahedra. Thus, the two forms differ in the relative amounts of direct Ru-Ru and oxygen mediated Ru-O-Ru interactions. We find that they display distinctly different properties below approximately

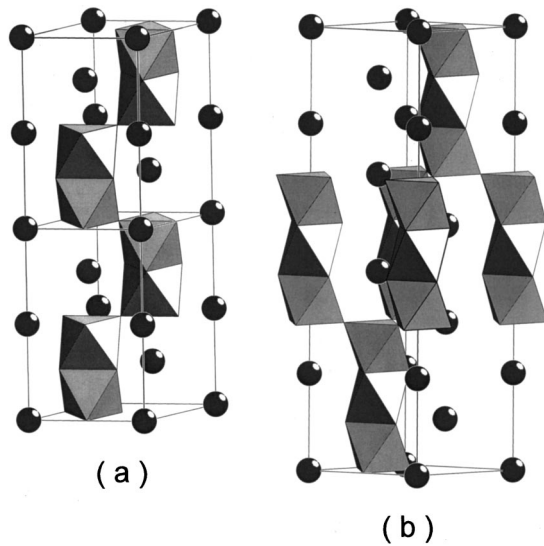


FIG. 1. Comparison of the crystal structures of the two crystallographic forms of BaRuO_3 . (a) four-layer phase, (b) nine-layer phase. The RuO_6 coordination octahedra are represented by geometrical figures (Ru at the center, O at corners), and the Ba as circles. The crystallographic cells are outlined.

100 K: the four-layer showing a metallic resistivity to low temperatures, and the nine-layer a subtle crossover to a more resistive state. Both show only weakly temperature-dependent magnetic susceptibilities with no indication of any local moment behavior for Ru. In addition, the nine-layer compound displays an increase in the magnetic susceptibility along one crystallographic direction (the c axis) at a temperature corresponding to the resistive crossover. The resistivity, specific heat and magnetic susceptibility of the nine-layer form have been reported earlier,¹⁰ though not as a function of crystallographic direction. Those results are in general but not detailed agreement with ours, likely due to differences in synthetic conditions, as described further below.

Experiment. The thermodynamically stable phase of BaRuO_3 under normal laboratory conditions is the nine-layer phase. Consequently, that form can be prepared in large quantities by standard synthesis. This has not yet been possible for the four-layer phase. We have found that the four-layer phase can be prepared in good purity by single-crystal growth. Single crystals of the two forms of BaRuO_3 were prepared from powders of BaRuO_3 , RuO_2 , and CuO in the ratios 1:0:0 and 0:1:1 heated in air in a tenfold (molar) excess of BaCl_2 . Platinum crucibles covered with ceramic covers were employed for crystal growth. The nine-layer crystals were obtained in the CuO containing melt. The melt was heated to 1250 °C, soaked for 12 h, cooled to 1050 °C at 2 °C per hour, then to 950 °C at 2 °C per minute, and then furnace cooled to ambient temperature. Similarly, the four-layer crystals were obtained by heating the BaRuO_3 containing melt to 1275 °C for 12 h, and then following the same cooling procedure. Some flux evaporation was observed during the growth processes. In both preparations, crystals were separated from the remaining flux by washing with warm H_2O and methanol in an ultrasonic bath. Powder x-ray diffraction patterns from both batches, taken by grinding large numbers of crystals together, indicated that there was no measurable contamination of four-layer crystals in the nine-layer batch, and no measurable contamination of nine-layer

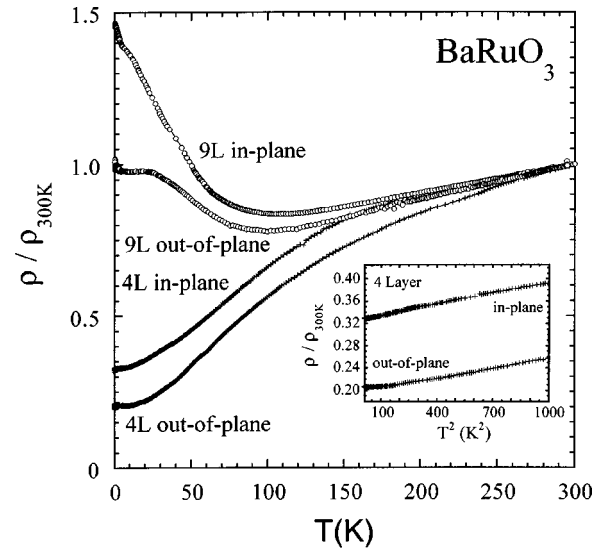


FIG. 2. The resistivities of single crystals of the nine-layer and four-layer crystallographic forms of BaRuO_3 for the in-plane and perpendicular-to-plane directions in the hexagonal crystals, normalized to their 300 K resistivities. Inset: the low-temperature resistivities of the four-layer phase plotted versus T^2 .

crystals in the four-layer batch. The single crystals of the four-layer phase formed thin plates with hexagonal basal plane sections, and those of the nine-layer phase were generally more equiaxed and had rhombic basal plane sections. In both cases the crystals were relatively small, with largest dimensions between 0.5 and 2 mm. The synthesis of the four-layer crystals is not always reproducible. Further studies are presently underway to determine the critical synthetic parameters controlling the conditions for obtaining that phase, which is metastable under ordinary synthetic conditions. Elemental analysis by energy dispersive x-ray analysis in an electron microscope did not reveal the presence of measurable quantities of impurities in either crystal form. Elemental impurities at the level of hundreds of ppm could be present, however, in either preparation.

Resistivities were measured on single crystals by a standard four-wire technique, in a temperature range between 20 mK and 300 K, with the dc current flowing either parallel or perpendicular to the basal planes. Magnetic susceptibilities were measured between 2 and 400 K in a commercial SQUID magnetometer (Quantum Design) in applied fields up to 7 T. Samples for the susceptibility measurements consisted of several crystals mounted on a nonmagnetic substrate with their basal plane normals aligned.

Results. The electrical resistivities of single crystals of the four-layer and nine-layer forms of BaRuO_3 are summarized in Figs. 2 and 3. The resistivities have been normalized to their 300 K values in both figures to facilitate the comparison of the behavior. The resistivities at 300 K for the four-layer phase are approximately 400 $\mu\Omega$ cm in the basal plane and 550 $\mu\Omega$ cm perpendicular to the plane. Similarly, for the nine-layer form, the resistivities at 300 K are approximately 350 $\mu\Omega$ cm in the plane and 160 $\mu\Omega$ cm perpendicular to the plane. Figure 2 shows the distinct difference in the resistive behavior for the two forms. The four-layer phase maintains its metallic behavior to low temperatures, while the nine-layer variant shows at first a metallic resistivity with decreasing temperature, but then a crossover to a more resistive

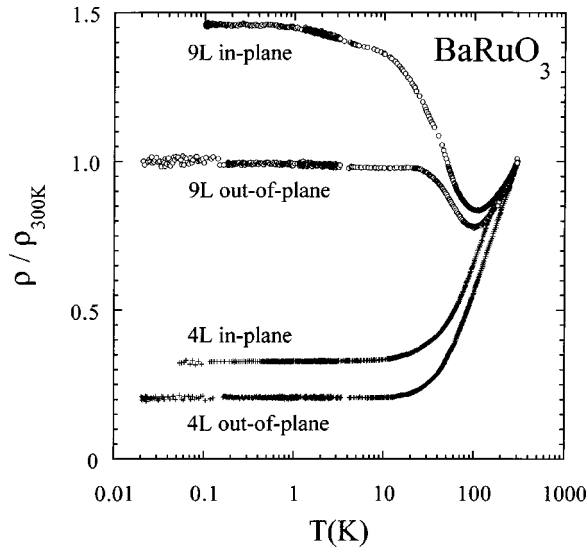


FIG. 3. The resistivities of single crystals of the nine-layer and four-layer BaRuO₃ crystals in two characteristic directions plotted in a semilog representation to illustrate the low-temperature behavior.

phase at low temperatures. Measurements on several crystals show that the temperature of this upturn is sample dependent. For both phases, Fig. 2 shows that the materials are only modestly anisotropic. The inset to Fig. 2 shows that the resistivity of the four-layer variant follows approximately the form $\rho = \rho_0 + AT^2$ at low temperatures along both characteristic directions. The values of A are $2.5 \times 10^{-3} \mu\Omega \text{ cm/K}^2$ and $3.4 \times 10^{-3} \mu\Omega \text{ cm/K}^2$ for in-plane and out-of-plane directions, respectively, and thus scale with the values of the resistivities at room temperature. The semilog plot, Fig. 3, illustrates the behavior of the resistivities to low temperatures. For the four-layer phase, residual resistivities on the order of $100 \mu\Omega \text{ cm}$ are measured in both characteristic directions. It is also seen that the resistivity of the nine-layer phase does not continue to rise below 10 K but rather saturates to a maximum value. These saturation temperatures are approximately 10 K perpendicular to the basal plane and approximately 1 K in plane, respectively. No superconductivity is observed down to the lowest measurement temperatures (<0.1 K).

The magnetic susceptibilities are summarized in Fig. 4. They are seen to be small and paramagnetic, and only weakly temperature dependent, consistent with the full loss of local moment of the Ru ions. Similar to the electrical resistivities, the magnetic susceptibility is not dramatically different for the two crystallographic directions for the four-layer phase. (For all curves shown, a very small free-moment-like contribution was subtracted, corresponding to an unpaired spin equivalent of a fraction of a percent.) We interpret the susceptibility as due to Pauli paramagnetism of the conduction electrons. The observed susceptibility of $\sim 7 \times 10^{-4} \text{ emu/mol}$, within the standard free-electron model, would indicate a rather high density of states at the Fermi level, corresponding to a linear term in the specific heat (γ) of up to 50 mJ/mol K^2 . The linear term can be lower if the susceptibility is enhanced by spin fluctuations. Interestingly, this estimate is consistent with the prefactor of the T^2 term in the resistivity assuming it is dominated by electron-electron scattering; i.e., a γ of 50 mJ/mol K^2 corresponds to a coefficient A in the range 10^{-3} to

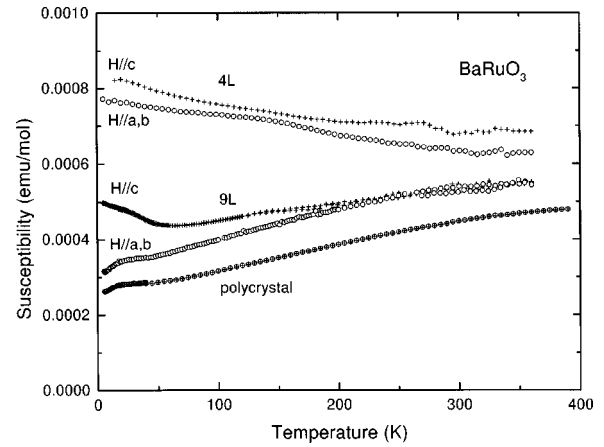


FIG. 4. The magnetic susceptibilities of single crystals of nine-layer and four-layer BaRuO₃ in in-plane and perpendicular-to-plane directions. Included for comparison are data for randomly oriented polycrystalline powder of the nine-layer phase synthesized by conventional methods.

$10^{-2} \mu\Omega \text{ cm/K}^2$,^{11,12} consistent with what is observed. There is no indication of an electronic transition at low temperatures. For the nine-layer phase, the susceptibility is equivalent to that of the four-layer phase at 400 K but then decreases smoothly to approximately half that value by 4.2 K. Following the above rationale, the average value of the susceptibility would correspond to linear term in the specific heat of up to 30 mJ/mol K^2 . Comparing this with the directly measured specific heat result,¹⁰ one concludes that the susceptibility for this phase is enhanced by a factor of 3–4. The lower density of states of the nine-layer form is consistent with what is to be expected from stronger direct Ru-Ru wave-function overlap, and therefore the presence of wider bands.

Although both nine-layer and four-layer BaRuO₃ are essentially paramagnetic with no local moment, a subtle behavior seen in the nine-layer material is worth mentioning. For fields along the c axis only, the susceptibility increases slightly below ~ 50 K in a form reminiscent of ferromagnetism. Indeed, this upturn depends on the applied field and is larger for smaller fields. From a systematic study we find a minute ferromagnetic component in the magnetization, corresponding to $\approx 10^{-4} \mu_B$. This very small moment is aligned along the c axis. As shown in Fig. 4, a similar, but less pronounced effect is measured in single-phase powder samples of this phase made under conventional synthetic conditions.¹³ Considering the different methods employed to prepare the polycrystalline and single-crystal samples, and the direction dependence in the single crystals, one would not expect this ferromagnetic contribution to come from an impurity phase. We are not aware of a Ba-Ru-O phase with a ferromagnetic T_c near 50 K, although one cannot rule out minute amounts of an unknown intergrowth phase. This apparent low-temperature magnetic transition will be studied in more detail in future work.

A further demonstration of the difference between the two forms of BaRuO₃ can be seen in their response to annealing treatment. Single crystals of both forms were annealed under flowing N₂ or O₂ gas for 4 days at 450 °C. The long time, low-temperature anneals test whether oxygen nonstoichiometry and crystalline perfection influence the properties. The temperature-dependent resistivities were measured after an-

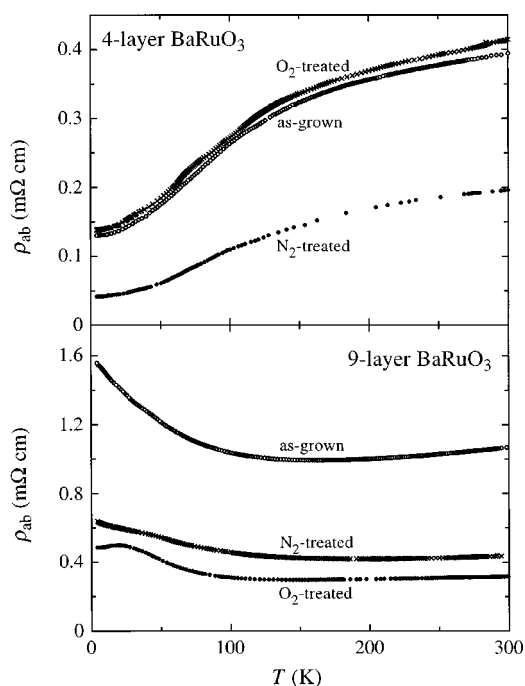


FIG. 5. The response of the basal plane resistivities of single crystals of nine-layer and four-layer BaRuO_3 to annealing in O_2 and N_2 at 450°C for four days. The data were obtained from different crystals.

nealing, shown in Fig. 5. The data indicate that the resistivity of the nine-layer phase shows dramatic changes for both the N_2 and O_2 anneals. The upturn in the resistivity at low temperature is suppressed after the anneals. In the case of the O_2 anneal, a metallic behavior is found at low temperatures after the occurrence of a broad peak. For the four-layer phase, the O_2 anneal has no apparent effect, whereas the N_2 anneal appears to decrease the resistivity substantially. The similar response of the nine-layer phase to annealing in both N_2 and O_2 suggests that the change in properties may not be due to the uptake or loss of very small amounts of oxygen but rather to the annealing out of some form of crystalline disorder. Either the nine-layer crystals grow with an intrinsically larger degree of structural disorder than do the four-layer crystals (highly unlikely due to the metastability of the latter), or the nine-layer phase is much more electronically sensitive to the presence of small amounts of disorder. For the four-layer phase, the difference between the N_2 and O_2 anneals suggests that an oxygen loss has been induced in the N_2 anneal, leading to decreased resistivity. Further study is needed to determine the effects of annealing more fully.

Conclusion. The two forms of BaRuO_3 , with identical chemical composition but different crystalline structures, display qualitatively different transport properties. The nine-layer phase shows metallic temperature-dependent resistivity at high temperatures, characterized by a linear dependence. At an intermediate temperature, which is somewhat sample dependent, the resistivity increases again slightly, and finally levels at lowest temperatures. For the four-layer phase, metallic resistivity is maintained to low temperatures in both the in-plane and out-of-plane directions, to a minimum residual resistivity of approximately $100 \mu\Omega \text{ cm}$ at low temperatures. The residual resistivity, due to impurity scattering, appears to be relatively high, in comparison, for example, to superconducting Sr_2RuO_4 single crystals.^{1,2} The resistivity follows approximately a T^2 law in both directions at low temperatures in the four-layer phase, indicating that the resistivity may be dominated by strongly correlated Fermi-liquid behavior. The coefficient of the T^2 term is consistent with the density of states approximated from the magnetic susceptibility data. The temperature dependence of the resistivity of the nine-layer variant of BaRuO_3 is highly unusual. After an initially metallic behavior, a transition to a more resistive state is observed, apparently accompanied by the development of a minuscule ferromagnetic moment.

Our annealing study has shown that the properties of the nine-layer phase appear to be particularly sensitive to the level of disorder in the sample. As similar temperature dependent resistivities are observed in the crystals made by other groups¹⁰ and in polycrystalline samples of this phase,¹³ it appears that the transport properties of the nine-layer phase are particularly sensitive to the presence of impurity atoms or perhaps disorder. This, along with the absence of local moment behavior, suggests a qualitative similarity to Sr_2RuO_4 . It would be of interest to pursue the characterization of the present materials further to see whether very high-purity preparations may show superconductivity. If the electronic states are indeed analogous in Sr_2RuO_4 and four-layer and/or nine-layer BaRuO_3 , then one would have to conclude that the layered structure of the latter compound is not what gives rise to its exotic magnetic and electronic state.

One of us (Y.L.) would like to acknowledge useful discussions with Darrell Schlom. The work at Pennsylvania State University was supported in part by NSF Grant No. ECS-9705839, and at Princeton University in part by NSF Grant No. DMR94-00362.

¹Y. Maeno *et al.*, *Nature* (London) **372**, 532 (1994).

²Y. Maeno, *Physica C* **282–287**, 206 (1997).

³J. J. Randall and R. Ward, *J. Am. Ceram. Soc.* **81**, 2629 (1959).

⁴A. Callaghan *et al.*, *Inorg. Chem.* **5**, 1572 (1966).

⁵J. M. Longo *et al.*, *J. Appl. Phys.* **39**, 1327 (1992).

⁶R. J. Bouchard and J. L. Gillson, *Mater. Res. Bull.* **7**, 873 (1972).

⁷R. J. Cava *et al.*, *J. Solid State Chem.* **116**, 141 (1995).

⁸P. Donahue *et al.*, *Inorg. Chem.* **4**, 306 (1965).

⁹S.-T. Hong and A. W. Sleight, *J. Solid State Chem.* **128**, 251 (1997).

¹⁰M. Shepard *et al.*, *J. Appl. Phys.* **81**, 4978 (1997).

¹¹K. Kadowaki and S. B. Woods, *Solid State Commun.* **58**, 507 (1986).

¹²K. Miyake *et al.*, *Solid State Commun.* **71**, 1149 (1989).

¹³J. R. Rijnssenbeek *et al.*, *Phys. Rev. B* (to be published).