1-22-2013

Class of Ferromagnetic Semiconductors

Larysa Shlyk  
*University of Kentucky*

Sergiy A. Kryukov  
*University of Kentucky*, kryukoff@gmail.com

Lance E. De Long  
*University of Kentucky*, delong@pa.uky.edu

Barbara Schüpp-Niewa

Rainer Niewa

Right click to open a feedback form in a new tab to let us know how this document benefits you.

Follow this and additional works at: [https://uknowledge.uky.edu/physastron_patents](https://uknowledge.uky.edu/physastron_patents)  
Part of the [Astrophysics and Astronomy Commons](https://uknowledge.uky.edu/physastron_patents), and the [Physics Commons](https://uknowledge.uky.edu/physics_commons)

**Recommended Citation**

Shlyk, Larysa; Kryukov, Sergiy A.; De Long, Lance E.; Schüpp-Niewa, Barbara; and Niewa, Rainer, "Class of Ferromagnetic Semiconductors" (2013). *Physics and Astronomy Faculty Patents*. 2.  
[https://uknowledge.uky.edu/physastron_patents/2](https://uknowledge.uky.edu/physastron_patents/2)

This Patent is brought to you for free and open access by the Physics and Astronomy at UKnowledge. It has been accepted for inclusion in Physics and Astronomy Faculty Patents by an authorized administrator of UKnowledge. For more information, please contact UKnowledge@lsv.uky.edu.
CLASS OF FERROMAGNETIC SEMICONDUCTORS

Inventors: Larysa Shlyk, Lexington, KY (US); Sergly Alexandrovich Kryukov, Lexington, KY (US); Lance Eric De Long, Lexington, KY (US); Barbara Schüpp-Niewa, Hallbergmoos (DE); Rainer Niewa, Hallbergmoos (DE)

Assignee: University of Kentucky Research Foundation, Lexington, KY (US)

Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 760 days.

Appl. No.: 12/062,076
Filed: Apr. 3, 2008

Prior Publication Data

Related U.S. Application Data
Provisional application No. 60/921,641, filed on Apr. 3, 2007.

Int. Cl.
C01G 55/00 (2006.01)
C01G 23/00 (2006.01)
C01G 23/04 (2006.01)

U.S. Cl. 252/62.62; 252/62.51 R; 252/62.3 R; 117/944; 257/421; 423/593.1; 423/594.6; 423/594.2; 423/598; 423/594.9; 423/594.16

Field of Classification Search 252/62.62, 252/62.51 R, 62.3 R; 423/593.1, 594.6, 594.2, 423/598, 594.9, 594.16; 117/944; 257/421

See application file for complete search history.

ABSTRACT

Single crystal and polycrystal oxomurhenates having the generalized compositions (Ba,Sr)2-xFe2CoRu(1-x/2)O15+(1-x/2) (1≤(x+y)≤5; 0≤z≤1) and (Ba,Sr)2-xFe2CoRu(1-x/2)O15+(1-x/2) (M=Fe,Co) belong to a novel class of ferromagnetic semiconductors with applications in spin-based field effect transistors, spin-based light emitting diodes, and magnetic random access memories.

15 Claims, 18 Drawing Sheets
PUBLICATIONS
Larysa Shlyk et al., High-Temperature Ferromagnetism and Tunable Semiconductivity of (Ba, Sr)M$_{24}$Ru$_{40}$O$_{111}$ (M=Fe, Co): A New Paradigm for Spintronics, Advanced Materials, published online Mar. 18, 2008, 9999, pp. 1-6.
Barbar Schipp-Niewa et al., $\text{BaFe}_{3} \text{Ru}_{2} \text{O}_{11.5}$, and $\text{BaCo}_{4} \text{Ru}_{3} \text{O}_{11.5}$, Preparation Crystal Structures, and Magnetic and Transport Properties of Quaternary Transition Metal Oxoruthenate, Z. Naturforsch, 62b, Jun. 2007, pp. 753-758.
* cited by examiner
\[ M(1) = \text{Fe}_{0.64}\text{Ru}_{0.36} \]
\[ \text{Co}_{0.10}\text{Ru}_{0.90} \]

\[ M(2) = \text{Fe}_{0.37}\text{Ru}_{0.63} \]
\[ \text{Co}_{0.22}\text{Ru}_{0.78} \]

FIG. 3
$T = 300 \text{ K}$

$H_c = 275 \text{ Oe}$

**FIG. 7c**
FIGURE 10a

BaFe$_{x+y}$Ru$_{2-y}$O$_{11}$
single crystal
$T = 300$ K
$H \perp ab$
CLASS OF FERROMAGNETIC SEMICONDUCTORS

CROSS REFERENCE TO RELATED APPLICATIONS

The present invention claims priority to U.S. Provisional Patent Application Ser. No. 60/921,641, filed Apr. 3, 2007, the entire disclosure of which is herein expressly incorporated by reference.

BACKGROUND AND SUMMARY OF THE INVENTION

From time to time new materials are discovered that serve as a basis for new or improved technologies with substantial commercial value in the marketplace. In the present day, there is considerable interest in discovering new materials for the development of spin-transport electronics (“spintronics”), in which the spin of charge carriers is exploited to provide enhanced functionality for microelectronic devices. In particular, the development of room-temperature ferromagnetic semiconductors comprises a central part of an ongoing, intensive effort to develop spin-based field effect transistors, spin-based light emitting diodes, and magnetic random access memory. If suitable novel classes of materials can be developed to underpin these new devices, they would enable a revolution in electronics and information technologies.

Ferromagnetic semiconductors are possibly the most intensively studied materials for spintronics applications. GaAs and ZnO doped with 3d elements are now widely studied as prototypical ferromagnetic semiconductors. The ideal ferromagnetic semiconductor material preferably has the following basic characteristics at room temperature:

1) Semiconducting gap of order 0.1-0.3 eV;
2) Ferromagnetic state with an ordered moment of at least 0.05 μB per formula unit;
3) Carrier concentration (10^{15}-10^{18}/cm^3) sufficient to provide a useful spin current;
4) Carrier mobility on the order of 10^{-2}-10^{-4} cm^2 V^{-1} s^{-1};
5) Moderate ferromagnetic coercive field (200-500 Oe) to facilitate switching of spin polarization; and
6) Compatibility with commercial substrate materials such as Si or Al_{2}O_{3}.

One obstacle to the implementation of spin-polarized semiconductor devices is the absence of suitable room-temperature, soft ferromagnetic semiconductors (FS’s). Dilute magnetic semiconductors are under intense study for applications in spintronics. However, the weak solubility of randomly placed magnetic ions in the semiconductor host makes these materials unsuitable for devices. It is, therefore, desirable to develop a room-temperature FS based on a periodic array of magnetic ions.

We have found that ternary and other complex ruthenium ferrites exhibit long-range ferromagnetic order well above room temperature, accompanied by narrow gap semiconducting properties that include a large anomalous Hall conductance, low resistivity, and high carrier concentration. Additionally, the physical properties can be tuned by simple chemical substitution of two elements, Fe and Co, or by varying the relative concentration of 3d and 4d elements within a homogeneity range that we have established. These promising properties—manifest within a single structural family—provide a fertile ground for fundamental studies and open up a host of potential device applications.

One inventive composition according to the present invention possesses a high ferromagnetic ordering temperature T_{c} that we have shown can be freely tuned from 300 to 500 K by doping. This material is semiconducting with an approximate gap of 200 meV. The coercive field at T=300 K is nearly ideal at H_{c}~275 Oe. X-ray data show that samples are single phase, and single crystals are obtainable. These initial results indicate that this material is a viable candidate for spintronic devices.

Further, we have synthesized another closely related metallic ferromagnet with extremely small coercive field (1-7 Oe) at T=80 K. This value is the same as for permalloy Ni_{80}Fe_{20}, which is a widely used metallic soft ferromagnet. It is particularly noteworthy that both of these inventive materials have the same crystal structure, which should facilitate the fabrication of composite heterostructures using these otherwise distinctly different materials.

We wish to emphasize that the new compositions come from a class of materials that are absolutely distinct from the GaAs and ZnO materials studied by other laboratories. The inventive compositions are not a “diluted magnetic semiconductors,” which usually suffer from clustering of magnetic ions among random lattice sites. Rather, the magnetic ions in these materials reside on a periodic lattice. Thus, we have discovered an entirely new paradigm for ferromagnetic semiconductors with the potential for widening this class into an ensemble of interesting, compatible materials having a range of physical properties with commercial potential.

Compositionally, the materials discussed above belong to a class of materials known as oxoruthenates. Oxoruthenates have attracted recent attention due to their electronic and magnetic properties. Advantageous properties of these materials include, for example, the occurrence of unconventional superconductivity, metamagnetism and itinerant ferromagnetism. A large number of ternary and multinary ruthenates can be described in perovskite structures and variants thereof.

One general feature is the occurrence of octahedrally-coordinated Ru connected with additional tetrahedrally-coordinated metal species.

According to the present invention, large single crystals of strontium and/or barium ruthenates containing a further transition metal from the third period of the periodic table have been grown with the aim of elucidating the crystal structures and magnetic properties of these attractive compounds, with a particular focus on the interdependence of magnetic properties and chemical composition.

According to one embodiment, the invention relates to single crystal and/or polycrystal oxoruthenates having the generalized composition \( (Ba_{x}Sr_{1-x})M_{x}Ru_{y}O_{z+0.5} \) (1≤x≤5; 0≤y≤1; M=Fe, Co). According to a further embodiment, the inventive oxoruthenates have the generalized composition \( (Ba_{x}Sr_{1-x})Fe_{y}Co_{x}Ru_{y}O_{z+0.5} \) (1≤(x+y)≤5; 0≤x≤1; when x=1 then y=0). In an embodiment, x=0, or y=0, and when x=0 then y=1. In another embodiment, the composition has a Curie temperature greater than or equal to about 300 K.

According to yet a further embodiment, the invention relates to single crystal oxoruthenates having a composition \( BaFe_{2+y}Ru_{y}O_{z+0.5} \) (x=1.4) and \( BaCo_{2+y}Ru_{y}O_{z+0.5} \) (x=0.2). The invention also relates to a broader range of ternary compositions, \( Sr_{2+y}Ru_{y}O_{z+0.5} \) (M=Fe, Co) and \( (BaSr)M_{2+y}Ru_{y}O_{z+0.5} \) (M=Fe, Co).

Black plate-like single crystals of quaternary transition metal oxoruthenates having the composition \( BaFe_{3+y}Ru_{y}O_{z+0.5} \) and \( BaCo_{1.8+y}Ru_{y}O_{z+0.5} \) (hexagonal, space group P6_3/mmc (No. 194), Fe: a=5.856(1), c=13.587(1) Ǻ, R1=0.029, wR2=0.084; Co: a=5.842(1), c=13.573(3) Ǻ, R1=0.033, wR2=0.075) have been grown from a BaCl_2 flux.

X-ray refinements and charge balance considerations suggest that Co^{2+} and mixed valence state Ru^{3+}Ru^{5+} and Fe^{2+/3}...
Fe$^{3+}$ are present in these compounds. Different occupations of the M(1) and M(2) sites by Ru and the 3d elements lead to deviations from the ideal compositions, BaM$_2$Ru$_4$O$_{11}$ and SrM$_2$Ru$_4$O$_{11}$; therefore, a homogeneity range (BaM$_{2-x}$Ru$_4$$_x$O$_{11}$ and SrM$_{2-x}$Ru$_4$$_x$O$_{11}$) has been discovered, which has important effects on physical properties. In one embodiment, the invention relates to a composition represented by the general formula BaM$_{2-x}$Ru$_4$$_x$O$_{11}$ wherein M=Fe and 0≤x≤1.4, or SrM$_{2-x}$Ru$_4$$_x$O$_{11}$ wherein M=Fe or Co and 0≤x≤1.4. Crystals grown from a BaCl$_2$ flux and/or a SrCl$_2$ flux according to the present invention are not restricted to a fixed composition.

Polycrystals of SrFe$_2$Ru$_4$O$_{11}$ or single crystals of SrFe$_2$Ru$_4$O$_{11}$, SrFe$_2$Ru$_4$O$_{11}$, and SrCo$_2$Ru$_4$O$_{11}$ were synthesized by solid-state reaction or grown from SrCl$_2$ flux. These compositions were confirmed by single crystal X-ray refinement and micro-probe analyses. Powder Rietveld refinement of the X-ray diffraction data were consistent with a composition of SrFe$_{3.5}$Ru$_{3.0}$O$_{11}$ (a=5.8375(4), c=13.403(1) Å).

The crystal structures contain two crystallographic sites with mixed Fe/Co and Ru occupation of different levels in octahedral coordination, and one site purely occupied by the respective 3d-metal. The latter is in trigonal bipyramidal coordination, with some indication of a displacement of the metal cation towards tetrahedral coordination. According to the charge balance, the ruthenium is incorporated with different electronic situations in the two Ru-containing sites. The Co compound may be described as containing Co$^{2+}$ and Ru$^{4+}$ next to Ru$^{3+}$Magnetic susceptibility data support this assignment.

According to magnetization measurements on oriented crystals, BaCo$_{1.85(5)}$Ru$_{4.15(6)}$O$_{11}$ is a soft ferromagnetic material with low coercive field and a spontaneous magnetization below $T_c=105$ K. It behaves as an electric conductor. However, BaFe$_{3.95(5)}$Ru$_{2.05(5)}$O$_{11}$ is a narrow band semiconductor with ferrimagnetic ordering at $T_c=440$ K. Other objects, advantages and novel features of the present invention will become apparent from the following detailed description of the invention when considered in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic illustration of the crystal structure for (Ba,Sr)M$_2$Ru$_4$O$_{11}$ (M=Fe,Co);

FIG. 2 is a schematic illustration of the crystal structure for BaFe$_{3.95(5)}$Ru$_{2.05(5)}$O$_{11}$ and Co$_{1.85(5)}$Ru$_{4.15(6)}$O$_{11}$;

FIG. 3 shows the arrangement of coordination, polyhedra of transition metal Ba, and atoms in BaFe$_{3.95(5)}$Ru$_{2.05(5)}$O$_{11}$ and Co$_{1.85(5)}$Ru$_{4.15(6)}$O$_{11}$; and FIG. 4 is an optical micrograph of single crystals of strontium ferrites according to the present invention;

FIG. 5 shows the field-cooled (FC) dc-susceptibility in an external magnetic field, $\mu_0$H=0.05 T ($H\|c$), for BaCo$_{1.85(5)}$Ru$_{4.15(6)}$O$_{11}$. The inset shows the inverse magnetic susceptibility vs. temperature. The solid line is a fit of the data to the Curie-Weiss law;

FIG. 6 shows the inverse magnetic susceptibility vs. temperature in an external magnetic field, $\mu_0$H=0.05 T ($H\|c$), for BaCo$_{1.85(5)}$Ru$_{4.15(6)}$O$_{11}$. The inset shows the temperature dependence of the resistivity ($\rho$ab-plane). The arrow designates the temperature of magnetic ordering at $T_c=105$ K;

FIG. 7(a) shows the FC dc-susceptibility in an applied magnetic field, $\mu_0$H=0.01 T ($H\|c$), for BaFe$_{3.95(5)}$Ru$_{2.05(5)}$O$_{11}$. The inset shows the temperature dependence of the resistivity ($\rho$ab-plane);

FIG. 7(b) is a plot of the FC dc-susceptibility in an applied magnetic field for BaFe$_{3.95(5)}$Ru$_{2.05(5)}$O$_{11}$. The inset shows the temperature dependence of the resistivity;

FIG. 7(c) is a plot of the magnetic moment vs. applied magnetic field, $H$, for BaFe$_{3.95(5)}$Ru$_{2.05(5)}$O$_{11}$;

FIG. 8(a) shows the temperature dependence of the FC dc magnetic susceptibility $\chi(T)$ for single-crystal SrFe$_{3.95}$Ru$_{2.05}$O$_{11}$ for H//ab and H//ab plane at applied magnetic field $\mu_0$H=0.1 T. $\chi(T)$ for polycrystalline SrFe$_2$Ru$_4$O$_{11}$ is also shown. Inset shows the magnetic moment m vs. H at 300 K;

FIG. 8(b) shows the temperature dependence of the FC dc magnetic susceptibility for single-crystal SrFe$_{3.95}$Ru$_{2.05}$O$_{11}$ for H//ab and H//ab plane at applied magnetic field $\mu_0$H=0.1 T. Inset shows the magnetic moment m vs. H at 280 K;

FIG. 9 shows the temperature dependence of the FC dc magnetic susceptibility for single-crystal SrFe$_{3.95}$Ru$_{2.05}$O$_{11}$ for H//ab and H//ab plane at applied magnetic field $\mu_0$H=0.1 T. Inset shows $\chi(T)$ for polycrystalline SrFe$_2$Ru$_4$O$_{11}$;

FIG. 10(a) is a plot of the low-field magnetic moment m vs. applied field H for single-crystal BaFe$_{3.95}$Ru$_{2.05}$O$_{11}$ at T=300 K with H//ab yielding a coercive field $H_c=92$ Oe. Inset shows the moment m vs. field ($H\|ab$, easy direction) at 5 K;

FIG. 10(b) is a plot of the moment m, vs. field ($H\|ab$, hard direction) at 300 K. Insets show low-field magnetic hysteresis at T=300 K with H//ab yielding $H_{c1}=480$ Oe (upper left) and moment m, vs. field ($H\|ab$) at 5 K (lower right);

FIG. 11(a) is a plot of the temperature dependences of the magnetic susceptibilities $\chi(T)$ for BaCo$_{1.85(5)}$Ru$_{4.15(6)}$O$_{11}$ and SrCo$_{2.05(5)}$Ru$_{2.05(5)}$O$_{11}$ single crystals in an applied field $H=500$ Oe. Filled and unfilled symbols indicate H//ab and H//ab-plane, respectively. Inset shows the inverse magnetic susceptibilities $\chi_c(T)$. Solid lines are fits to the Curie-Weiss law;

FIG. 11(b) is a plot of the moment m, vs. field ($H\|ab$, easy direction) at 5 K for BaCo$_{1.85(5)}$Ru$_{4.15(6)}$O$_{11}$ and SrCo$_{2.05(5)}$Ru$_{2.05(5)}$O$_{11}$ single crystals. Inset shows the moment m, vs. field ($H\|ab$, hard direction);

FIG. 12 is a plot of the temperature dependence of resistivity $\rho(T)$ for BaFe$_{3.95}$Ru$_{2.05}$O$_{11}$ and SrFe$_{2.05}$Ru$_{2.05}$O$_{11}$ single crystals. Filled and unfilled symbols correspond to electrical current H//ab, and H//ab, respectively. Inset shows $\rho(T)$ for polycrystalline SrFe$_2$Ru$_4$O$_{11}$ and single-crystal SrFe$_2$Ru$_4$O$_{11}$;

FIG. 13 is a plot of $\rho(T)$ for single-crystal BaCo$_{1.85(5)}$Ru$_{4.15(6)}$O$_{11}$ (H//ab). Inset shows $\rho(T)$ for single-crystal SrCo$_{2.05(5)}$Ru$_{2.05(5)}$O$_{11}$. Arrows designate the magnetic ordering temperature $T_c$;

FIG. 14 is a plot of magnetic field dependence of the Hall resistivity $\rho_{xy}(H)$ for single-crystal SrFe$_2$Ru$_4$O$_{11}$ at 280 and 300 K. The sharp change in slope at 0.1 T (anomalous Hall effect) is evident of electron spin-polarization. Inset shows $\rho_{xy}(H)$ for single-crystal BaFe$_3$Ru$_2$O$_{11}$ at $T=300$ K;

FIG. 15 is a plot of $\rho_{xy}(H)$ for single-crystal SrCo$_2$Ru$_2$O$_{11}$ at $T=150$ and 5 K. Inset shows $\rho_{xy}(H)$ for single-crystal BaCo$_{1.85(5)}$Ru$_{4.15(6)}$O$_{11}$ at 5 K (below $T_c$) and at 120 K (above $T_c$). Note the anomalous contribution vanishes at $T=120$ K; and

FIG. 16 is a plot of cobalt concentration dependence of the Curie temperature $T_c$ and semiconducting gap $\Delta$ for polycrystalline SrFe$_{3.95}$Ru$_{2.05}$O$_{11}$ solid solutions having nominal compositions 0≤x≤1, x=0. The inset shows Fe concentration dependence of $T_c$, and $\Delta$ for SrFe$_{3.95}$Ru$_{2.05}$O$_{11}$ ($x=0$, 0.8 single crystals, x=1 polycrystal). Solid lines are linear fits to the data.
Detailed Description of the Drawings

Crystal Structure and Composition

Selected data on the crystal structure determinations and refinements for crystals having inventive compositions according to the present invention are shown in Tables 1 and 2. With reference to FIGS. 1 and 2, Ba and O form a distorted hexagonal close-packing motif, with Ba consequently located in anti-cuboctahedral coordination by O. Ru and Fe/Co occupy octahedral and trigonal bipyramidal interstices of this packing exclusively formed by O.

In FIGS. 1-3, layers of M(2)O₆ octahedra (lighter octahedra) are connected in the [001] direction via pairs of octahedra M(1)O₆ (darker octahedra) and trigonal prisms FeO₆ or CoO₆ (dark polyhedra), respectively. Ba (large pale spheres) is located within the layers of pairs of double octahedra and trigonal prisms. Occupation parameters for M(1) and M(2) are given. Emphasized polyhedra are drawn with displacement ellipsoids (99% probability, data from Fe compound).

FIG. 4 is an optical micrograph of strontium ferrite single crystals according to the present invention.

### Table 1

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>BaFe₃₂₉₃Ru₂₆₅₅O₁₁</th>
<th>BaCo₂₈₀₀Ru₁₄₅₅O₁₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal size, mm³</td>
<td>0.08 x 0.05 x 0.001</td>
<td>0.05 x 0.03 x 0.001</td>
</tr>
<tr>
<td>Crystal system</td>
<td>hexagonal</td>
<td>hexagonal</td>
</tr>
<tr>
<td>Space group</td>
<td>P6₃/mmc</td>
<td>P6₃/mmc</td>
</tr>
<tr>
<td>a, Å</td>
<td>5.856 (1)</td>
<td>5.842 (1)</td>
</tr>
<tr>
<td>c, Å</td>
<td>13.587 (1)</td>
<td>13.573 (3)</td>
</tr>
<tr>
<td>V, Å³</td>
<td>403.5</td>
<td>398.2</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>D, calculated, g cm⁻³</td>
<td>6.32</td>
<td>7.02</td>
</tr>
<tr>
<td>μ (Magnetic Moment, mm⁻¹)</td>
<td>15.5</td>
<td>16.3</td>
</tr>
<tr>
<td>F(000), e</td>
<td>695.3</td>
<td>753.0</td>
</tr>
<tr>
<td>hkl range</td>
<td>a₁, a₂, a₃</td>
<td>a₁, a₂, a₃</td>
</tr>
<tr>
<td>2θ, max., deg</td>
<td>55.85</td>
<td>55.72</td>
</tr>
<tr>
<td>Refl. measured</td>
<td>6001</td>
<td>5996</td>
</tr>
<tr>
<td>Refl. unique</td>
<td>217</td>
<td>216</td>
</tr>
<tr>
<td>Rₓ</td>
<td>0.045</td>
<td>0.047</td>
</tr>
<tr>
<td>Param. refined</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>R(F)/R(W(F))</td>
<td>0.029/0.084</td>
<td>0.035/0.075</td>
</tr>
<tr>
<td>(all reflections)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GoF (F²)</td>
<td>1.413</td>
<td>1.053</td>
</tr>
<tr>
<td>Δρₘ₀, (max/min), eA⁻³</td>
<td>1.30</td>
<td>0.86</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Chemical Structure parameters for BaFe₂₉₃Ru₂₆₅₅O₁₁ (first row of parameters) and BaCo₂₈₀₀Ru₁₄₅₅O₁₁ (second row of parameters, in italics)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>Ba(1)</td>
</tr>
<tr>
<td>M(1)*</td>
</tr>
<tr>
<td>M(2)*</td>
</tr>
<tr>
<td>Fe(3)</td>
</tr>
<tr>
<td>Co(3)</td>
</tr>
<tr>
<td>O(1)*</td>
</tr>
<tr>
<td>O(2)*</td>
</tr>
</tbody>
</table>

*For BaFe₂₉₃Ru₂₆₅₅O₁₁: M(1) = 0.64 (2) R² = 0.30 Rn; M(2) = 0.37 (1) R² = 0.63 Rn, for BaCo₂₈₀₀Ru₁₄₅₅O₁₁: M(1) = 0.14 (2) R² = 0.59 Rn; M(2) = 0.22 (1) R² = 0.70 Rn.

Two crystallographic positions are mixed-occupied by M and Ru in different ratios and surrounded octahedrally by O, localized in the centers of 10 of 24 available octahedral holes of the hexagonal packing (inclusive those formed with participation of Ba). In every third layer, ½ of the octahedral holes are occupied by M(2) forming layers of edge-sharing octahedral. These layers are interconnected in the third dimension by M(1)O₆ octahedra, which share faces with the unoccupied octahedra within the layers. The M(1)O₆ octahedra themselves share faces, leading to pairs of octahedra.

Within the layers with M(1) sites (two out of three layers) only ½ of the octahedral holes are occupied. In this way, the pairs of octahedra are not directly interconnected, but are separated by the barium ions. As a remarkable feature of the structure, O(3) as a part of the close packing connects four octahedra via vertices, but does not coordinate to Ba. The crystal structure is completed by sites purely occupied by Fe or Co. These d-metal species are in a trigonal bipyramidal configuration surrounded by O (i.e., in voids of two face-sharing tetrahedra) oriented within the layer of the pairs of octahedra.

Earlier refinements based on powder diffraction data indicated small mixing between Ru in this position, but the data presented do not indicate any increased electron density. In the refinement in space group P6₃/mmc, this transition metal atom is located on a mirror plane. Close inspection of the displacement parameters reveal elongation of the close packing in the [001] direction and indicate a dislocation in the sense of a preference for a tetrahedrally-coordinated position rather than a five-fold coordinated site. Analyses of single crystal X-ray diffraction data collected on the Fe-containing crystal at 150 K did not give any indication of an enhancement of displacement of the Fe site in question.

In the exemplary compositions BaFe₂₉₃Ru₂₆₅₅O₁₁ and BaCo₂₈₀₀Ru₁₄₅₅O₁₁, different levels of occupation of the two sites M(1) (Fe₆₄₋ₓRuₓ₆₄₋ₓ) or Co₆₄₋ₓRuₓ₆₄₋ₓ and M(2) (Fe₃₋ₓRuₓ₆₃₋ₓCoₓ₆₃₋ₓRuₓ₆₃₋ₓ) with Ru and M=Fe, Co, as compared to literature reports, lead to compositions deviating from the ideal compositions BaFe₆₄Ru₆₄O₁₁ and BaCo₆₄Ru₆₄O₁₁. Homogeneity ranges in the sense of Ba₂Ru₄O₁₁ can be obtained. For M=Fe the formation from refinement of X-ray diffraction data results in BaFe₂₉₃Ru₂₆₅₅O₁₁, in contrast to an approximate composition of BaFe₂Ru₄O₁₁ from µ-probe.

Comparably small isotropic displacements parameters for the M(1) and M(2) position in the refinement of the diffraction data may suggest a somewhat higher occupation with Ru, also indicated by the fact that the result from µ-probe exactly...
matches the molar ratio used in the preparation. X-ray powder
diffraction patterns showed only weak reflections of an
unknown second phase (unit cell parameters from powder
least squares refinements: a = 5.830(1), c = 13.582(5) Å) and
are strongly textured according to (001) as may be expected
from the hexagonal platelet shape of the crystals.

As an important conclusion, the studied crystals clearly do
not represent the composition BaFe₄Ru₄O₁₁, but contain a
significantly higher molar ratio n(Fe)/n(Ru). However, for
M=Co the composition obtained from the structure refine-
ments with Ba₃Co₂Ru₄O₁₁ exactly matches the composition
found from μ-probe with BaCo₄Ru₂O₆ and shows a minor but significant deviation from the ideal compo-
sition in direction of a smaller ratio n(Co)/n(Ru).

Distances between Ba and O are in the range permitted for
highly coordinated Ba. Distances d(M-O) are slightly shorter
in the Co compound as compared to the Fe compound as a
result of the higher occupation with Ru in high oxidation state
in the Co compound. Distances d(Co₃-O₂), however, are
longer than d(Fe₃-O₂) as one would expect for low oxidation
state low spin atoms. Selected interatomic distances are
shown in Table 3.

<table>
<thead>
<tr>
<th>TABLE 3</th>
</tr>
</thead>
</table>
| Selected bond lengths (Å) for BaFe₄₃Ru₄O₁₁ (first values) and
BaCo₄₃Ru₄O₁₁ (second values, in italics) with estimated
standard deviations in parentheses. |

<table>
<thead>
<tr>
<th></th>
<th>Ba(1)</th>
<th>M(1)</th>
<th>M(2)</th>
<th>M(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O(1)</td>
<td>O(1)</td>
<td>O(1)</td>
<td>O(1)</td>
</tr>
<tr>
<td></td>
<td>2.836(3)</td>
<td>2.922(3)</td>
<td>1.996(2)</td>
<td>1.834(5)</td>
</tr>
<tr>
<td></td>
<td>2.825(3)</td>
<td>2.926(3)</td>
<td>1.978(4)</td>
<td>1.860(4)</td>
</tr>
<tr>
<td>d</td>
<td>2.652(2)</td>
<td>2.652(1)</td>
<td>2.013(4)</td>
<td>2.003(4)</td>
</tr>
<tr>
<td></td>
<td>6 x</td>
<td>3 x</td>
<td>4 x</td>
<td>3 x</td>
</tr>
<tr>
<td></td>
<td>O(1)</td>
<td>O(1)</td>
<td>O(1)</td>
<td>O(1)</td>
</tr>
<tr>
<td></td>
<td>1.996(2)</td>
<td>1.978(4)</td>
<td>2.013(4)</td>
<td>2.003(4)</td>
</tr>
<tr>
<td>d</td>
<td>1.5 x</td>
<td>1.5 x</td>
<td>1.5 x</td>
<td>1.5 x</td>
</tr>
<tr>
<td></td>
<td>O(2)</td>
<td>O(2)</td>
<td>O(2)</td>
<td>O(2)</td>
</tr>
<tr>
<td></td>
<td>2.073(4)</td>
<td>2.013(4)</td>
<td>2.013(4)</td>
<td>2.003(4)</td>
</tr>
<tr>
<td>d</td>
<td>3 x</td>
<td>3 x</td>
<td>3 x</td>
<td>3 x</td>
</tr>
<tr>
<td></td>
<td>O(3)</td>
<td>O(3)</td>
<td>O(3)</td>
<td>O(3)</td>
</tr>
<tr>
<td></td>
<td>2.036(4)</td>
<td>2.003(4)</td>
<td>2.013(4)</td>
<td>2.003(4)</td>
</tr>
<tr>
<td>d</td>
<td>3 x</td>
<td>3 x</td>
<td>3 x</td>
<td>3 x</td>
</tr>
<tr>
<td></td>
<td>O(4)</td>
<td>O(4)</td>
<td>O(4)</td>
<td>O(4)</td>
</tr>
<tr>
<td></td>
<td>2.262(8)</td>
<td>2.268(8)</td>
<td>2.268(8)</td>
<td>2.268(8)</td>
</tr>
<tr>
<td>d</td>
<td>2 x</td>
<td>2 x</td>
<td>2 x</td>
<td>2 x</td>
</tr>
</tbody>
</table>

The distance d(Ru—Ru) within the pairs of octahedra
is believed to be indicative of the oxidation state of ruthenium.
For the present crystal structures, we have to consider
the possibility of Ru in different oxidation states for sites M(1)
(face-sharing octahedron) and M(2) (no face sharing) because
intermediate as well as mixed valence situations have been
observed for oxoruthenates. In the Fe-containing compound,
the distance was refined to d(M(1)—M(1)) = 2.760(2) Å. This
distance is located at the short end of the range for which one
would expect an oxidation state of +5.5 for Ru. Within the
frame of simple charge balance calculations, and provided
that an oxidation state of +5 is valid for Ru on the M(2) site
(no face sharing with other occupied octahedra) for the
composition from structure refinements BaFe₄₃Ru₄O₁₁, this
would lead to an oxidation state close to +2 for Fe. However,
with an occupation of M(1) with 0.64(1) Fe and
0.36 Ru this distance is highly dominated by Fe—Fe and
Fe—Ru contacts and does not necessarily give valuable
information about pure Ru—Ru interactions. For BaCo₄₃Ru₄O₁₁
the situation is reversed: with an occupation of the site M(1)
with 0.10(1) Co and 0.90 Ru the distance d(M(1)—M(1)) = 2.625(2) Å can be viewed as close to a pure
Ru—Ru distance, but without any metal-metal bonding. This
value is at the lower end expected for Ru in an oxidation state
of +5. The charge balance then leads to Co close to +2 if M(2)
contains Ru in the oxidation state +3. This result is in good
agreement with the magnetic susceptibility data that is dis-
cussed hereafter.

Magnetic Properties

The magnetic susceptibility measurements of a Ba
Co₁₅₆₄₀Ru₄₁₅₆₄₀O₁₁ single crystal reveal a spontaneous
magnetization below Tₘ = 105 K (FIG. 5). This material can be
considered a soft ferromagnetic material with low coercive
field. Both BaCo₁₅₆₄₀Ru₄₁₅₆₄₀O₁₁ and BaFe₁₅₆₄₀Ru₄₂₁₅₆₄₀O₁₁
contain ferromagnetically-aligned Co (Fe) and Ru
moment, which leads to overall ferromagnetic order via
superexchange through the oxygen atoms. As shown in the
 inset of FIG. 5, the inverse of the field-cooled (FC) dc-sus-
ceptibility (Hdc) exhibits an abrupt change in slope above
100 K and a linear behavior above 120 K. A Curie-Weiss fit of
the data in the temperature interval 120 K < T < 300 K gives a
Weiss constant θ = 70 K and an effective magnetic moment of
2.41 μ₆. The susceptibility of the single crystal BaCo₁₅₆₄₀Ru₄₁₅₆₄₀O₁₁
is strongly anisotropic and is much higher for
H // c Above 150 K the susceptibility follows a modified
Curie-Weiss law with a temperature-independent term
χₒ ≈ 3 × 10⁻⁴ mol / emu, θ = 115 K, and μₑ = 2.41 μ₆ (FIG. 6). Fitting
with a spatial average χₘ(Γₙ, Γ₋ₙ, V₃) of the Curie-
Weiss law above 150 K yields a magnetic moment of 2.81 μ₆, which is in good agreement with the experimental
result. This can be taken as support for the previous oxidation state discussion. The temperature dependence of the
FC dc-susceptibility BaFe₄₃Ru₄O₁₁ shows that in this sample ferrimagnetism develops below
T₀ = 440 K (FIG. 6(a)). Due to the very high Curie temperature of the compound, we are not able to extract the parameters
of magnetic interactions from a high temperature fit of the
reciprocal susceptibility to the Curie-Weiss law.

As noted above, additional dc measurements on a sample
having the composition BaFe₄₃Ru₄O₁₁ show semiconducting behavior (approximate gap of 200 meV, and a coercive field at 300 K of about 275 Oe). These data are shown in FIGS. 7(b) and 7(c).

The temperature dependences of the magnetic susceptibility
X(T) of single-crystal SrFe₄₃Ru₄O₁₁ (FIG. 8(a)) and
SrFe₄₃Ru₄CoO₁₁ (FIG. 8(b)) (H // ab and H // c planes) reveal
ferromagnetic or possibly ferromagnetic) transition anomalies
at Curie temperatures Tₘ = 400 and 300 K, respectively. These results indicate that the Curie temperature of the strontium ferrites strongly increases with higher iron content,
which is verified by a very high Tₘ = 488 K observed for
poly-crystalline SrFe₄₃Ru₄O₁₁ (FIG. 8(a)). The inset to FIG.
8(a) shows the magnetic moment m vs. H at 300 K, and the inset to FIG. 8(b) shows m vs. H at 2800 K. The arrows designate the magnetic ordering temperature, Tₘ.

Low-field magnetization data reveal strong magnetization
anisotropy m⊥//m ∼ 300 for SrFe₄₃Ru₄O₁₁ at T < 5 K, which
indicates an easy axis perpendicular to the ab plane. M(H)
curves exhibit typical ferromagnetic hysteresis without satu-
ration in fields of up to 5.5 T for both field directions. Small coercive fields Hc ≈ 10 Oe are observed for
SrFe₄₃Ru₄O₁₁ at T = 280 K, and modest anisotropy with
Hc ∼ 350 Oe and H⊥ ∼ 500 Oe for SrFe₄₃Ru₄CoO₁₁ at T = 300 K.

Since the ionic radius of Ba²⁺ is larger than that of Sr²⁺,
substitution of Ba for Sr results in an increase of lattice
dimensions, and it is reasonable to expect that the magnetic
interactions in a given barium ferrite are weaker than those of the strontium analog. Indeed, this expectation is borne out by
the magnetic susceptibilities of single-crystal BaFe$_{1-x}$Ru$_x$O$_{3+y}$ (T$_c$=440 K) and polycrystalline SrFe$_{5}$Ru$_{3}$O$_{11}$ (T$_c$=488 K, with a similar composition) shown in FIG. 9. BaFe$_{1-x}$Ru$_x$O$_{3+y}$ is a soft ferromagnet with saturation moment $\mu_{sat}$=1.25 $\mu_B$/f.u., and coercive fields H$_c$=480 Oe and H$_c$=92 Oe at T=300 K (FIGS. 10(a) and 10(b)). We observe more than two orders of magnitude reduction in magnetization anisotropy (m$_m$=1.5 at T=5 K) for BaFe$_{1-x}$Ru$_x$O$_{3+y}$ compared to SrFe$_{5}$Ru$_{3}$O$_{11}$.

Substitutions of Co for Fe result in lower Curie temperatures, as shown by FC $\chi$(T) data for BaCo$_{1-x}$Ru$_x$O$_{3+y}$ and SrCo$_{5}$Ru$_{3}$O$_{11}$ single crystals for which magnetic order develops below T$_c$=105 K and T$_c$=115 K, respectively (FIG. 11(a)). Above 150 K, both BaCo$_{1-x}$Ru$_x$O$_{3+y}$ and SrCo$_{5}$Ru$_{3}$O$_{11}$ follow modified Curie-Weiss laws having positive Weiss constants (Table 4), which is consistent with possible ferromagnetic interlayer and intralayer exchange couplings. Fitting with a spatial average $\chi=(\chi_{z}+\chi_{y})/3$ of the Curie-Weiss susceptibilities above 150 K yields effective magnetic moments, $\mu_{eff}=2.78 \mu_B$ (BaCo$_{1-x}$Ru$_x$O$_{3+y}$) and $\mu_{eff}=2.84 \mu_B$ (SrCo$_{5}$Ru$_{3}$O$_{11}$) near the values 2.81 $\mu_B$ (BaCo$_{1-x}$Ru$_x$O$_{3+y}$) and 2.74 $\mu_B$ (SrCo$_{5}$Ru$_{3}$O$_{11}$) obtained using theoretical spin-only values for Ru$_{3}$O$_{11}$ (S=3/2), Ru$_{2}$O$_{11}$ (S=5/2) and Co$^{2+}$ (S=3/2). We found that the easy magnetization direction changes from axial to in-plane for BaCo$_{1-x}$Ru$_x$O$_{3+y}$ and SrCo$_{5}$Ru$_{3}$O$_{11}$. These compounds are very soft ferromagnets with saturation moments $\mu_{sat}=1.8 \pm 0.1$ $\mu_B$/f.u. at T=5 K (see Table 4 and FIG. 11(b)).

**TABLE 4**

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T_c$ (K)</th>
<th>$\mu_{eff}$ (µB)</th>
<th>$\theta_c$ (K)</th>
<th>$H_c$ (Oe)</th>
<th>$H_{max}$ (Oe)</th>
<th>$\mu_{sat}$ (µB)</th>
<th>m$_m$/m$_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrFe$<em>{5}$Ru$</em>{3}$O$_{11}$</td>
<td>300</td>
<td>10 (280K)</td>
<td>10 (280K)</td>
<td>300 (SK)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrFe$<em>{5}$Ru$</em>{3}$O$_{11}$</td>
<td>400</td>
<td>350 (300K)</td>
<td>500 (300K)</td>
<td>26 (SK)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrFe$<em>{5}$Ru$</em>{3}$O$_{11}$</td>
<td>488</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrCo$<em>{5}$Ru$</em>{3}$O$_{11}$</td>
<td>115</td>
<td>2.84</td>
<td>106</td>
<td>122</td>
<td>150</td>
<td>120</td>
<td>1.9 (SK)</td>
</tr>
<tr>
<td>BaFe$<em>{5}$Ru$</em>{3}$O$_{11}$</td>
<td>440</td>
<td>92</td>
<td>300 (SK)</td>
<td>480 (300K)</td>
<td>1.5 (300K)</td>
<td>15 (SK)</td>
<td></td>
</tr>
<tr>
<td>BaCo$_{1-x}$Ru$<em>x$O$</em>{3+y}$</td>
<td>105</td>
<td>2.78</td>
<td>115</td>
<td>70</td>
<td>200 (SK)</td>
<td>2 (SK)</td>
<td>1.7 (SK)</td>
</tr>
</tbody>
</table>

*polybarystalline sample; all others are single crystal.

Electric Conductivity

The different 3d- (Co, Fe) and 4d-metal (Ru) contents can be used to tailor the electronic properties. Our results indicate that the ratio of 3d- and 4d-magnetic ions plays an important role in determining the Curie temperatures of strontium ferrites, and that a higher Fe/Ru ratio correlates with higher $T_c$.

Measurements of the electrical resistivity reveal that the Co-poor phase BaCo$_{1-x}$Ru$_x$O$_{3+y}$ (15$\%$ Ru$_{3}$O$_{11}$) is an electrical conductor (inset to FIG. 6), while the Fe-rich phase BaFe$_{5}$Ru$_{3}$O$_{11}$ is a narrow band semiconductor (inset to FIG. 7). The respective compounds with ideal compositions, BaFe$_{5}$Ru$_{3}$O$_{11}$ and BaCo$_{1-x}$Ru$_x$O$_{3+y}$, have both been described as poor metals, since they exhibit very weak semiconductor-like temperature dependence of the resistance in measurements taken on pressed pellets of polycrystalline material.

The difference in the resistivity behavior of the Co- and Fe-containing samples may be a consequence of different electronic structures of these metals. As a possible explanation, we suggest that the presence of an extra electron in BaCo$_{1-x}$Ru$_x$O$_{3+y}$ closes a gap at the Fermi surface of BaFe$_{5}$Ru$_{3}$O$_{11}$.

Materials with 3d magnetism tend to have low magnetic anisotropy and often exhibit soft magnetic behavior. Therefore, the high anisotropy of these compounds may originate from an incompletely quenched orbital angular momentum of the relatively large Ru 4d-orbitals. A strong decrease in magnetic anisotropy is observed for larger substitutions of Fe for Ru, suggesting that the Fe/Ru ratio reduces the spin-orbit interaction responsible for the anisotropy. On the other hand, complete substitution of Fe$^{3+}$ (3d electronic configuration) by Co$^{2+}$ (3d electronic configuration), leads to an evolution of the easy axis from axial for BaFe$_{5}$Ru$_{3}$O$_{11}$ to planar for BaCo$_{1-x}$Ru$_x$O$_{3+y}$ to planar for BaCo$_{1-x}$Ru$_x$O$_{3+y}$.

The temperature dependences of the resistivities $\rho$(T) of the Fe-based barium- and strontium-ferrites are shown in FIG. 12; and the slopes $\rho$=0/ΔT=0 indicate semiconductivity for all compositions. The in-plane resistivity of single-crystal BaFe$_{5}$Ru$_{3}$O$_{11}$ increases by one order of magnitude as the temperature falls from 300 to 5 K, while corresponding increases of about two and four orders of magnitude are observed for single-crystal SrFe$_{5}$Ru$_{3}$O$_{11}$ and polycrystalline SrFe$_{5}$Ru$_{3}$O$_{11}$, respectively. At temperatures above 180 K, $\rho$(T) obeys an activated form $\rho=\rho_0 e^{\Delta/E}$ with narrow gaps $\Delta$=34 (20 meV for current parallel (p//)) or perpendicular (p//) to the ab-plane for single-crystal BaFe$_{5}$Ru$_{3}$O$_{11}$. For the case of the Sr analogues, $\Delta$=36 meV for parallel current in single-crystal SrFe$_{5}$Ru$_{3}$O$_{11}$, and we estimate an average $\Delta$=59 meV for polycrystalline SrFe$_{5}$Ru$_{3}$O$_{11}$. The fact that the resistivity of the polycrystalline sample is higher than the single crystals suggests that the resistance of the polycrystalline sample is dominated by carrier scattering at the grain boundaries.
ten greater than found in a barium counterpart, and depends critically on the preparation procedure; values ranging from 0.03 to 0.1 Ω cm may be found under various conditions of temperature and atmosphere.

Since the value of the room-temperature resistivities of both barium and strontium ferries studied here are low and typical of semiconductors, these materials have potential to optimize the spin injection and detection efficiencies across a S/FS interface.

The in-plane and out-of-plane resistivities ($\rho_{\parallel,\perp}$=$3.9 \times 10^{-4}$ Ω cm and $\rho_{\perp,\parallel}$=1.4$\times 10^{-5}$ Ω cm, respectively) of single-crystal BaCo$_3$Ru$_2$O$_{11}$ differ from the Fe analogues in that they are metallic (d$p$/dT=0) (FIG. 13). The resistivities are large (of order 300 μΩ cm), indicating that (p(T) is strongly affected by the Ru/Co disorder in the sample. The ferromagnetic phase transition is marked by a small drop-off of p(T) at −105 K. Above 105 K, the in-plane resistivity displays a strong linear temperature dependence. This behavior is similar to one of the defining characteristics of high-temperature cuprate superconductors, and is considered a signature of strongly correlated or marginal Fermi liquid phases.

The resistivity of single-crystal SrCo$_2$Ru$_2$O$_{11}$ differs by rising with changing slope as temperature decreases below $T_c$. The estimated gap is very small (~1.1 meV) and is reduced below the magnetic ordering temperature. The differences in electron transport between Co- and Fe-containing ferries may be attributed to the stronger hybridization of Co$^+$ (3d$^4$) and mixed Ru$^{4+}$/Ru$^{6+}$ (4d$^3$/4d$^4$) states via superexchange through the oxygen O$^{2-}$2p-orbitals in BaCo$_3$Ru$_2$O$_{11}$. This leads to a wider conduction band relative to BaFe$_2$Ru$_2$O$_{11}$, in which Fe$^{3+}$ is in a 3d$^5$ configuration with one less electron. On the other hand, SrCo$_2$Ru$_2$O$_{11}$ exhibits a higher $T_c$ and remains a semiconductor with a very narrow gap compared to metallic BaCo$_3$Ru$_2$O$_{11}$, Hall coefficient measurements reveal the predominant charge carriers in single-crystal BaFe$_2$Ru$_2$O$_{11}$, and SrFe$_2$Ru$_2$O$_{11}$ are holes (FIG. 14). The Hall resistivity in ferromagnets $\rho_{xy}$=R$_H$(4$\pi$M) where R$_H$ is the Hall coefficient resulting from the Lorentz force on the carriers, and R$_H$ is the anomalous Hall coefficient that is dependent upon the magnetization and spin-orbit coupling. Therefore, $\rho_{xy}$ has roughly the same field dependence as the magnetization in ferromagnets below $T_c$. This behavior is demonstrated by single-crystal BaFe$_2$Ru$_2$O$_{11}$ and SrFe$_2$Ru$_2$O$_{11}$ in FIG. 14, which shows $\rho_{xy}$ has a large field dependence for H<1.0 T and $T$<<$T_c$, where the anomalous contribution dominates. This is highly suggestive of a strong, net electron-spin polarization that is requisite for an ideal FS impacting contact.

For BaFe$_2$Ru$_2$O$_{11}$ above 1.0 T, the magnetization saturates and $\rho_{xy}$ becomes much less field dependent with $\rho_{xy}$=1$\times$10$^4$ cm$^2$/V/1/sec, where c is the electron charge, c is the speed of light, and n is the carrier concentration. The slope of $\rho_{xy}$-H curve at $T$=300 K and $\mu$=1.0 T yields n=2$\times$10$^{21}$ cm$^{-3}$ with mobility $\mu_{xy}$=R$_H$/n=4$\times$10$^4$ V cm$^{-1}$/sec. The anomalous contribution to the Hall effect of BaFe$_2$Ru$_2$O$_{11}$ at $T$=300 K is ~70μΩ cm, which is much larger than those of metallic or semiconducting ferromagnets such as (Ga,Mn)As and FeCoSi. We have found that the anomalous term of SrFe$_2$Ru$_2$O$_{11}$ remains quite sizeable at $T_c$. An extension of the anomalous term to temperatures above $T_c$ is also observed in other ferromagnetic semiconductors such as (Ga,Mn)As, and may be indicative of short-range magnetic order.

The Hall effects observed for single-crystal BaCo$_3$Ru$_2$O$_{11}$ and SrCo$_2$Ru$_2$O$_{11}$ are distinctly different from the Fe-based ferries, as is apparent in FIG. 15. The negative slope of $\rho_{xy}(T)$ indicates that the dominant charge carriers are electrons in the Co-analogues, and there is a two order-of-magnitude difference between the low-field $\rho_{xy}$ of the BaFe$_2$Ru$_2$O$_{11}$ and BaCo$_3$Ru$_2$O$_{11}$ samples at 5 K. No anomalous Hall signal is observed at $T>T_c$, and $\rho_{xy}$ varies linearly with magnetic field for the Co-analogues. A carrier concentration n=3$\times$10$^{20}$ cm$^{-3}$ and mobility $\mu_{xy}$=55 cm$^2$/V/1/sec can be estimated from the ordinary Hall coefficient at $T$=120 K for BaCo$_3$Ru$_2$O$_{11}$, while n=1$\times$10$^{21}$ cm$^{-3}$ and $\mu_{xy}$=21 cm$^2$/V/1/sec at 150 K for SrCo$_2$Ru$_2$O$_{11}$.

An especially attractive characteristic of ternary ruthenium ferries is that the magnetic and electrical properties of these materials can be widely varied by exchange of Fe with Ru over a homogeneity range of (Ba,Sn)Fe$_2$Ru$_2$O$_{11}$, or Co for Fe within (Ba,Sn)Fe$_2$Co$_{2-x}$Ru$_2$O$_{11}$ solid solutions. In both cases, the substitution of Fe$^{3+}$/Ru$^{5+}$ for Ru$^{4+}$/Ru$^{3+}$ or Fe$^{3+}$/Fe$^{2+}$ for Co$^{2+}$ can be used to control the ferromagnetic and transport properties. In one embodiment, the invention relates to a composition represented by the general formula Ba(Sn)$_{x}$Co$_{3-x}$Ru$_2$O$_{11}$, wherein 0.5<0.5<1, and $T_c$=1.4 K, or Sr(Sn)$_{x}$Co$_{2-x}$Ru$_2$O$_{11}$, wherein 0.5<0.5<1, and $T_c$=1.4.

These compositional degrees of freedom allow us to study the fundamental physics behind the magnetic and electric properties over a wide compositional range without any accompanying structural changes. For example, the Co- or Fe-concentration dependencies of $T_c$ and the gap $\Delta$ of poly-crystalline Sr(Sn)$_{x}$Co$_{3-x}$Ru$_2$O$_{11}$ and single-crystal Sr(Sn)$_{x}$Co$_{2-x}$Ru$_2$O$_{11}$, which are shown in FIG. 16. Increases of the Co$^{2+}$ (3d$^5$) concentration produce a continuous evolution from a high-temperature, p-type FS to a ferromagnetic metal. More importantly, these data demonstrate that the wider the semiconducting gap the higher the temperature of magnetic ordering. This intriguing trend is opposite to that observed for diluted magnetic semiconductors, where an increase in carrier concentration leads to higher $T_c$ but also to higher metallicity. The origin of this unique phenomenon in ferries is not clear at present, but we believe it is an important clue concerning the mechanisms of high-temperature ferromagnetism in these materials.

Ternary ruthenium ferries offer a new paradigm for spintronics. (Ba,Sn)Fe$_2$Co$_{2-x}$Ru$_2$O$_{11}$ are narrow-gap semiconductors with Curie temperatures at or above room temperature. The wide homogeneity ranges accessible via different 4d/3d-transition element compositions allow one to engineer desirable electrical transport properties and tune the strength of ferromagnetic interactions, anisotropy and $T_c$ within a single structure type. Moreover, it is important to have materials that can form heterostructures with a good lattice match, since lattice mismatch typically leads to low-quality interfaces that are detrimental to spin polarized transport.

Isostructural (Ba,Sn)(Fe$_{1-x}$Co$_x$)$_2$Ru$_2$O$_{11}$ solid solutions and the homogeneity range of (Ba,Sn)Fe$_2$Co$_{2-x}$Ru$_2$O$_{11}$ and (Ba,Sn)Co$_2$Ru$_2$O$_{11}$ provide a highly desirable situation in which the maximal lattice mismatch between the end members of these solutions does not exceed 0.2%. These novel materials therefore might be exploited to grow epitaxial thin films having different electrical and magnetic properties to form heterostructures for multifunctional devices in which the contributions of both electrons and holes play important roles.

**Experimental**

Sample Preparation

For preparation of BaFe$_{0.93}$Sn$_{0.07}$Ru$_2$O$_{11}$, 11.3 mmol BaCO$_3$, 3.40 mmol RuO$_2$ and 1.39 mmol Fe$_2$O$_3$ were mixed...
with about 1.5 g of BaCl₂, which was used as an agent to initiate crystal growth. The resulting powders were heated to 1350°C and kept at this temperature for 70 hr. Then the furnace was slowly cooled (~50°C/hr.) to room temperature. Black, hexagonal, single-crystalline platelets with maximal sizes of 2 mm and a thickness of about 0.05 mm were obtained.

Starting materials for BaCo₁₋₈₅(Ru₄₋₁₅)₂O₉ were 11.3 mmol BaCl₂, 3.40 mmol Ru₂O₃, and 1.30 mmol CO₂O₆. After addition of BaCl₂, this mixture was treated in the identical manner as for the Fe compound.

Single crystal samples of SrFe₂₉Ru₄ₐO₁₉ were prepared by mixing 0.26 mol. % Fe₂O₃, 0.52 mol. % Ru₂O₅, and 0.39 mol. % SrCl₂. The powder mixture was heated in air at ambient pressure to 1300°C and kept at this temperature for 50 hr. The furnace was cooled to 1000°C for 4 hr. and then switched off.

Polycrystals of SrFe₂₉Ru₄O₁₉ were synthesized by heating a mixture of stoichiometric amounts of SrCO₃, Ru₂O₅, and Fe₂O₃ to 1100°C for 15 hr. The furnace was cooled to room temperature at a rate of 100°C/hr.

Structure Determination

For X-ray diffraction intensity data collection, small black crystals with the shape of hexagonal platelets were selected. The measurements were performed on an Oxford Xc'elibur diffractometer equipped with a Graphite monochromator and a Sapphire CCD area detector at ambient temperature using MoKα radiation (Scans: Fe 360 images, α=4.0°, 5 s); Cu 416 images, α=1.0°, 1 s; Co 180 images, α=2.0°, 30 s; and 208 images, α=2.0°, 30 s).

The crystal of the Fe phase was additionally measured at 150 K to track a possible displacive phase transition to a non-centrosymmetric crystal structure. After empirical absorption correction, the structure solutions were successful with direct methods in space group P6₃/mmc (No. 194, centrosymmetric, program SHELXL-97-2). In the refinement procedure, oxygen atoms were chosen to be treated with isotropic displacement parameters due to limited number of unique intensity data (SHELXL-97-2). Selected information on the data collections, structure determinations and refinements is presented in Table 1. Table 2 gives positional parameters, site occupation numbers and displacement parameters.

Chemical Composition Determination

Chemical µ-probe analyses (JEOL JSM 5000LV at 20 kV and equipped with a Link AN 10000 detector system for EDX analysis) resulted in very stable compositions both for several different points on each investigated crystal, and for different crystals with the exact ratio n(Mn)/n(Fe)=6.0 for each measurement (average of 47 at. % Ru, 39 at. % Fe and 14 at. % Ba for BaFe₃₋ₓRuₓ₂O₉ (x=0.17); 60 at. % Ru, 11 at. % Co and 14 at. % Ba for BaCo₁₋₀₅₀Ru₁ₓ₀₅₀O₁₉). This result also applies for the same crystals measured on the diffractometer. No reliable quantification of the oxygen content is possible with this technique. No further elements were detected.

Magnetic Susceptibility and Electric Conductivity Measurements

The magnetic susceptibility χ(T) of oriented single crystals was measured between 2 K and 600 K in fields up to 5 T in a commercial SQUID magnetometer (Quantum Design). The electrical resistivity and Hall effect of the samples was measured in the temperature interval 1.8-300 K by using the four-probe dc method.

Although exemplary embodiments have been described above as heating single crystals materials to 1300°C, the temperature can range between 1280-1350°C. For polycrystalline materials, the temperature range can be between 1150-1300°C. The synthesis of these materials can be conducted in air or in a nitrogen atmosphere.

Although exemplary embodiments have been described above with particular compositions, it should be recognized that some elements can be substituted while still maintaining the above-described properties. For example, Mn can be substituted for Co or Fe, with the composition of BaMn₄Ru₂O₁₉ with a Tₛ ~200 K. Another compound could be SrRu₄Fe₂O₁₉ with a Tₛ ~148 K. Moreover, Ru could be substituted with Ti or Sn. For example, BaTi₄Fe₂O₁₉ and SrTi₄Fe₂O₁₉ with a Tₛ of approximately 200 K and BaSn₄Fe₂O₁₉ with a Tₛ ~180 K.

The foregoing disclosure, including the drawings, has been set forth merely to illustrate the invention and is not intended to be limiting. Since modifications, combinations and coregulations of the disclosed embodiments incorporating the spirit and substance of the invention may occur to persons skilled in the art, the invention should be construed to include everything within the scope of the appended claims and equivalents thereof.

What is claimed is:

1. A spinnontric component, comprising a ferromagnetic semiconductor material in the form of an epitaxial thin film and having a composition represented by the general formula: Ba₁₋ₓSrₓFe₂₋ₓₐCoₓRu₄₋ₓₐO₁₉, wherein 0≤x≤0.5, 0≤y≤5, 1≤(x+y)≤5 and 0≤z≤1, and when x=1 then y=0.
2. A component according to claim 1, wherein x=0, or y=0, and when x=0 then z=1.
3. A component according to claim 2, wherein the composition represented by the general formula: BaM₄Ru₂O₁₉, wherein M=Fe or Co and 0≤n≤1.4, or SrM₄Ru₂O₁₉, wherein M=Fe or Co and 0≤n≤1.4.
4. A component according to claim 3, wherein the semiconductor material is monocristalline.
5. A component according to claim 1, wherein the semiconductor material is polycristalline.
6. A component according to claim 1, wherein the semiconductor material has a Curie temperature greater than or equal to about 300 K.
7. A spinnontric component, comprising a ferromagnetic semiconductor material in the form of an epitaxial thin film and having a composition represented by the general formula: Ba₃₋ₓ₋₀₅₀Ruₓ₋₀₅₀Fe₀₂₋ₓ₋₀₅₀O₁₉, wherein 0≤y≤1, and 0≤n≤1.4, or Sr₃₋ₓ₋₀₅₀Ruₓ₋₀₅₀Fe₀₂₋ₓ₋₀₅₀O₁₉, wherein 0≤y≤1, and 0≤n≤1.4.
8. A method of making a ferromagnetic semiconductor material, comprising:
   forming a mixture comprising about 11.3 mmol BaCO₃, 3.4 mmol Ru₂O₃, 1.39 mmol Fe₂O₃ and 1.5 g BaCl₂;
   heating the mixture to about 1350°C for about 70 hours; and
   cooling the mixture to room temperature to form the semiconductor material.
9. A method of making a ferromagnetic semiconductor material, comprising:
   forming a mixture comprising about 11.3 mmol BaCO₃, 3.4 mmol Ru₂O₃, 1.30 mmol CO₂O₆ and 1.5 g BaCl₂;
   heating the mixture to about 1350°C for about 70 hours; and
   cooling the mixture to room temperature to form the semiconductor material.
10. A method of making a single crystal ferromagnetic semiconductor material, comprising:
    forming a mixture comprising about 0.26 mol.% Fe₂O₃, 0.52 mol.% Ru₂O₃, 0.39 mol.% SrCl₂;
    heating the mixture in air to about 1350°C for about 50 hours.
then heating the mixture in air at about 1000°C for 4 hours; and
cooling the mixture to room temperature to form the semi-
conductor material.

11. A ferromagnetic semiconductor material having a com-
position represented by the general formula: SrFe₃Co₃-
Ru₁₋ₓ₋₀₁, wherein 0 ≤ x ≤ 0.4 and M=Fe or
SrMₓFe₁₋ₓRu₁₋ₓ₋₀₁, wherein 0 ≤ x ≤ 0.4 and M=Fe or Co.

12. A ferromagnetic semiconductor material according to
claim 11, wherein x=0 or y=0.

13. A ferromagnetic semiconductor material having a com-
position represented by the general formula:

BaM₂₋ₓₐRuₓ₋₂₋₀ₓ₁, wherein 0 ≤ x ≤ 1.4 and M=Fe or
SrM₂₋ₓₐRuₓ₋₂₋₀ₓ₁, wherein 0 ≤ x ≤ 1.4 and M=Fe or Co.

14. A ferromagnetic semiconductor material having a com-
position represented by the general formula: Ba(Fe₁₋ₓ-
ₐCoₙ)₂₋ₓₐRuₓ₋₂₋₀ₓ₁, wherein 0 ≤ x ≤ 1.4 and 0 ≤ y ≤ 1, or Sr(Fe₁₋ₓ-
ₐCoₙ)₂₋ₓₐRuₓ₋₂₋₀ₓ₁, wherein 0 ≤ x ≤ 1.4 and 0 ≤ y ≤ 1.

15. A ferromagnetic semiconductor material having a com-
position represented by the general formula: SrFe₂Co₃-
Tiₓ₋₀₋₀ₓ₁₋₀, wherein 0 ≤ x ≤ 5, 0 ≤ y ≤ 5, and 1(x+y) ≤ 5.