Transitions in $Sr_2Ru_xIr_{1-x}O_4$ compounds studied by the ^{99}Ru Mössbauer effect

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The ^{99}Ru Mössbauer effect has been measured in the $Sr_2Ru_xIr_{1-x}O_4$ system for $x=1.0$, 0.7, 0.5, and 0.4 at 4.2 K. The isomer shift measurements show a change of $-0.05(.02)$ mm/s as the compound changes from a metal $(x=0.7)$ to an insulator $(x=0.5)$. This isomer shift change is the electronic signature of the metal-insulator transition. All these spectra are single line. At $x=0.4$ the compound undergoes a magnetic phase transition with the measurement of a hyperfine magnetic field of 7.2(1.5) T. The ^{99}Ru Mössbauer effect has been measured from 1.8 to 147.5 K for Sr_2RuO_4 and from these measurements the Debye temperature was estimated to be 427(50) K. [S0163-1829(99)03334-2]

INTRODUCTION

The compounds $Sr_2Ru_xIr_{1-x}O_4$ (Ref. 1) have been of interest because they are isostructural to the higher-temperature superconducting system $La_{2-x}Ba_xCuO_4$ system[2] and they mirror the system's multiple transitions. For $Sr_2Ru_xIr_{1-x}O_4$, $x=0.9$, the compound undergoes a phase change from a magnetic insulator to a metal (MI transition) and for $x=1$ and $T_c<0.93\,\mathrm{K}$, it is superconducting.[3] There are many intriguing aspects to these compounds. The superconductivity in these compounds is unconventional (not *s* wave) and most likely triplet.[4] They contain ruthenium and not copper, which has been a common element in most superconducting, layered compounds. Sr_2RuO_4 is superconducting on its own without doping of the Ru site as is not the case in the $La_{2-x}Ba_xCuO_4$ system.[5] Since ruthenium is not an impurity in the compound, this makes the use of ^{99}Ru Mössbauer effect (ME) spectroscopy a particularly useful local probe of the electronic properties.

It would normally be expected that all the $Sr_2Ru_xIr_{1-x}O_4$ compounds would be metallic since the $4d$ band is partially filled. But, this is not the case. The compounds change from a metal to an insulator as lr is added at $x=0.9$ and this continues until around $x=0.6$ where magnetic, resistive, and crystallographic measurements show an abrupt change in the properties of the compound.[6] Other structural changes have been observed between Sr_2RuO_4 and Sr_2lrO_4 through powder neutron diffraction measurements.[7,8] It is found that the MO_6 ($M=$Ru,Ir) octahedra have a regular configuration in the Ru compound but in the Ir compound the Ir-O octahehra are rotated by 11° about the *c* axis. ME measurements are very sensitive to structural and electronic changes[9] in compounds through the magnetic or electric quadrupole interaction, isomer shift interaction and the recoil free fraction. It is for this reason that the ^{99}Ru ME (Ref. 10) was chosen to investigate these compounds. In the present study we report measurements of the compounds $Sr_2Ru_xIr_{1-x}O_4$ where Ru is a natural constituent of the compound and not an impurity. ^{99}Ru measurements have been made for different compositions of the above compound: $x=0.2$, 0.4, 0.5, $x=0.7$, and $x=1.0$. It is found that the isomer shift measurement is sensitive to changes in x providing a signature of the metal-insulator transition between $x=0.5$ and $x=0.7$ and the compound undergoes a magnetic phase transition at $x=0.4$. Measurements were made of the recoil free fraction for Sr_2RuO_4 from 1.8 to 147.5 K and a Debye-Waller curve was plotted from the results. This yielded a Debye temperature of 427(50) K.

EXPERIMENTAL

Polycrystalline materials of $Sr_2Ru_xIr_{1-x}O_4$, with $x=0.2$, 0.5, 0.7, 1.0, were synthesized by Cava *et al.*[6] These authors

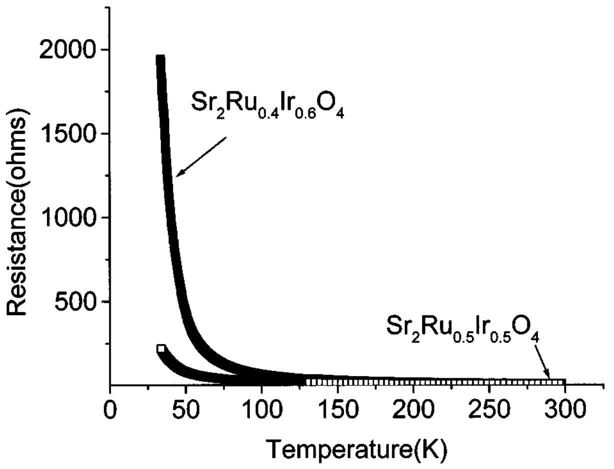

FIG. 1. Resistance versus temperature measurement for $Sr_2Ru_{0.4}Ir_{0.6}O_4$ and $Sr_2Ru_{0.5}Ir_{0.5}O_4$.

performed magnetic, x-ray and resistivity measurements on these compounds. In summary, the $x=0.2$, 0.5 and $x=0.7$ compounds show magnetic insulating behavior and the $x=1.0$ compound is a metal. These previous studies of the $Sr_2Ru_xIr_{1-x}O_4$ compounds showed small amounts of $SrRuO_3$ (50 ppm) and the intermediate compounds showed some end member phases. The ^{99}Ru ME spectrum of $SrRuO_3$ is magnetic with a hyperfine magnetic field[11] of 35 T. Its spectrum does not appear in any of the ME spectra of $Sr_2Ru_xIr_{1-x}O_4$. Large amounts of end member impurity phases would be determined by the presence of multiple lines in a ME spectrum and this was not observed.

A second set of polycrystalline $Sr_2Ru_xIr_{1-x}O_4$ samples with $x=0.4$ and $x=0.5$ were prepared by the method described earlier.[6] Powdered samples were annealed at 950 °C in oxygen for 8 h to produce pellets. Resistance versus temperature measurements are shown for these compounds in Fig. 1. The resistance measurements show that these samples follow insulating behavior at low temperature with the same order of magnitude change in resistance from $x=0.5$ to $x=0.4$ as the first set of samples.[6] X-ray measurements were made of both sets of samples at Oakridge National Laboratories. The measurements show that the d spacings for the major lines in the spectrum for the second set of samples, $x=0.4$ and $x=0.5$, are consistent with the first set of samples.

The sources, ^{99}Rh(Ru), for the ^{99}Ru ME were produced by proton irradiation at the University at Buffalo cyclotron of either natural ruthenium powder or powder composed of enriched isotopes ^{100}Ru and ^{101}Ru. The production mechanism proceeded through both (p,2n) and (p,3n) reactions on both targets. Targets were irradiated by a 5 μA beam of about 30 MeV protons to produce the necessary activity. ME experiments were originally performed on $Sr_2Ru_xIr_{1-x}O_4$ with $x=1.0$ and $x=0.7$ using natural ruthenium targets but no ME was found for the $x=0.5$ compound until enriched isotope targets were used to construct ME sources. The enriched isotope sources also enabled high temperature (147.5 K) measurements of the $x=1.0$ compound. In general, the enriched isotope sources were more active, produced about a factor of five less noise than the natural ruthenium sources, produced very little long lived activity and since they did not contain ^{99}Ru this also prevented resonance absorption in the sources. This preparation of the source is important because it extends the temperature range of the ^{99}Ru ME measurements beyond 78 and toward 200 K.

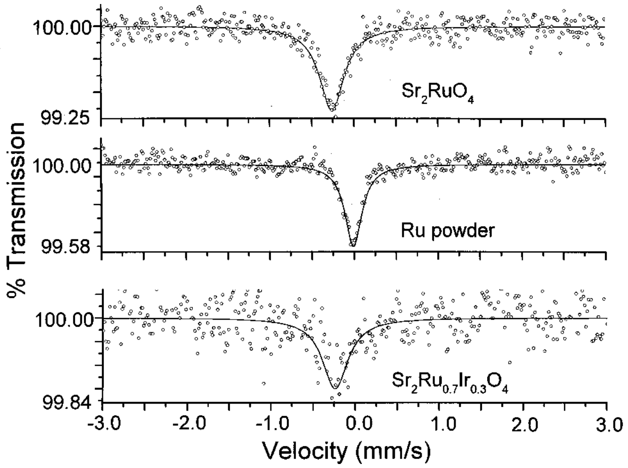

FIG. 2. Percent transmission versus velocity for the ME measurements of the source ^{99}Rh(Ru) versus different absorbers: Sr_2RuO_4, ruthenium powder, and $Sr_2Ru_{0.7}Ir_{0.3}O_4$. Both the source and the absorbers were measured at 4.2 K. The solid line is a Lorentzian line computer fit to the data (circles).

It was necessary to perform experiments with both the source and absorber at low temperature because of the low recoil free fraction associated with the 90 keV ME gamma ray. Transmission experiments using the 16-day half life ^{99}Rh(Ru) were performed using a probe that was designed at the University at Buffalo which allowed both the source and absorber to be at the same temperature. The probe was placed in a Janis (helium exchange) dewar specifically designed for Mössbauer spectroscopy. A 3 mm thick NaI detector was placed below the Mylar windows of the dewar to detect the ME gamma ray.

ME experiments were performed on both sets of samples of $Sr_2Ru_xIr_{1-x}O_4$ compounds at 4.2 K. The raw data was folded about the midpoint of the spectra and Lorentzian lines were fit to the data. Figures 2 and 3 are results from the first set of samples. Figure 2 is a set of measurements performed on the $x=1, x=0.7$ compounds and Ru powder. Figure 3 is a set measurements on the $x=1, x=0.5$ and RuO_2. The entire $Sr_2Ru_xIr_{1-x}O_4$ series of compounds show single lines, which are shifted relative to the ruthenium powder. Table I shows representative experimental linwidths, isomer shifts, and ruthenium mass per unit area.

Table I and Fig. 3 show that there is a change in the isomer shifts between the $x=0.5$ and $x=1.0$ compounds of -0.05 mm/s. This change in the IS is comparable to other ME phase change measurements such as the metal-insulator transition measured by the ^{57}Fe ME in V_2O_3.[12] The uncertainty in the line position, found by using a least squares program, makes the shift as low as -0.03 or as high as -0.07 mm/s. The isomer shift change between the $x=0.7$ and the $x=0.5$ compounds is slightly larger at $-0.06(0.02)$ mm/s and there is no measurable shift between the $x=1.0$ and the $x=0.7$ compounds as shown in Fig. 2 and Table I. Experiments were repeated and the uncertainty in measurement is shown in the parenthesis.

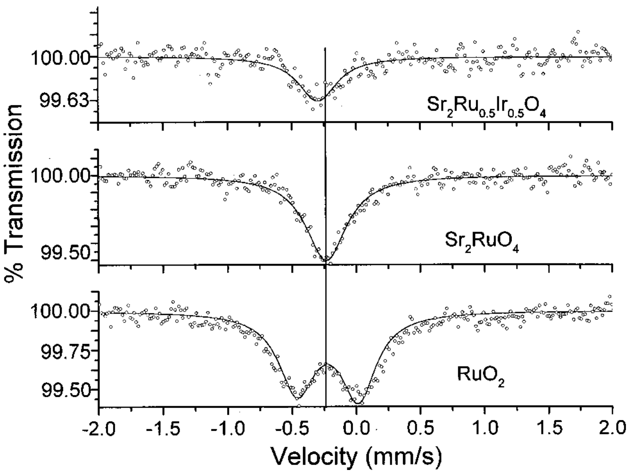

FIG. 3. Percent transmission versus velocity for the ME measurements of the source ^{99}Rh(Ru) versus different absorbers: Sr_2RuO_4, $Sr_2Ru_{0.5}Ir_{0.5}O_4$, and RuO_2. Both the source and absorbers were measured at 4.2 K. The solid line is a Lorentzian line computer fit to the data (circles). The vertical line is drawn to compare the isomer shifts of Sr_2RuO_4 and $Sr_2Ru_{0.5}Ir_{0.5}O_4$.

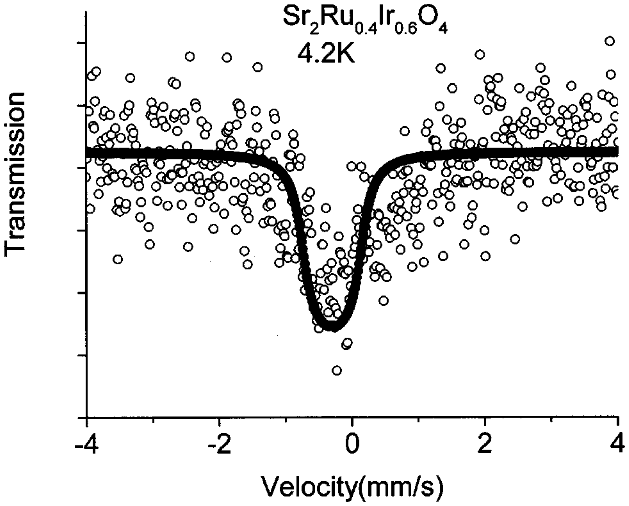

FIG. 4. Relative transmission versus velocity for the ME measurement of the source ^{99}Rh(Ru) and absorber $Sr_2Ru_{0.4}Ir_{0.6}O_4$ measured at 4.2 K. The open circles represent the folded data and the solid line represents the fit to the data.

Two sets of ^{99}Ru ME measurements were performed on the second set of $Sr_2Ru_xIr_{1-x}O_4$ samples with $x=0.4$ and $x=0.5$. Both measurements on the $x=0.5$ compound were performed with absorber samples which contained 75 mg/cm^2 of Ru while the $x=0.4$ absorbers contained 80 and 60 mg/cm^2. The ^{99}Ru ME measurement for the $x=0.5$ was consistent with the first set of samples. That is, the IS shift was the same within experimental error while the linewidth was broadened by about 10%. The $x=0.4$ sample showed a very broad line as shown in Fig. 4. The line was computer fit to the magnetic interaction for the ^{99}Ru ME. In the case of the ^{99}Ru ME magnetic interaction the mixed multipolarity of the gamma rays (E2 and M1) in the decay of ^{99}Rh is important. The mixing of E2 and M1 gamma rays results in 18 equally spaced lines with intensities determined by the mixing ratio, $\delta^2=2.7$, and the square of the proper Clebsch-Gordan coefficients for each line intensity.[10] A linewidth of 0.14 mm/s was used for all lines. The fit in figure 4 yields an $\mathrm{IS}=-0.30(.03)$ mm/s and a hyperfine magnetic field of 7.2(1.5) T. The 18 lines are unresolved from one another and hence there isn't any structure in the spectrum. A fit of the data to a quadrupole interaction was tried but it was not as consistent with the data as the magnetic interaction.

There was no sharp resonance recorded for $Sr_2Ru_{0.2}Ir_{0.8}O_4$. This is probably due to a combination of the following: (1) the small amount of ruthenium powder, (2) this same powder not occupying unique sites in the crystal, and (3) too much noise due to scattering of higher energy radiation from Ir (high $Z=77$) into the ME gamma ray window.

^{99}Ru ME measurements were made on Sr_2RuO_4 from 1.8 to 147.5 K. The temperature, measured by a calibrated diode attached to the sample, was controlled to within 0.1 K using a LakeShore temperature controller. The samples were in thermal contact with a nichrome wrapped wire metal ring. The natural logarithm of the normalized area (4.2 K) of the resonance curve is plotted versus the temperature in Fig. 5. The area was determined by subtracting the fitted area under the fitted resonance curve from the background line. The plot in Fig. 5 has the same form as DW curves for iron doped into superconductors.[13] It is constant at low temperatures and approximately linear at higher temperatures with no large deviations from straight-line behavior and therefore no anomalous changes in the phonon spectra at 1.8 K (near T_c) and above 130 K (where single crystal resistivity measurements show changes between ρ_{ab} and ρ_c). Nor was there a change in the isomer shift as a function of temperature. The slope of the higher temperature part of the plot in Fig. 5 was estimated to be constant and from this the Debye temperature Θ was found to be 427(50) K which is consistent with previous work.[1,14]

DISCUSSION

Systematic measurements[15] are established for ^{99}Ru isomer shifts which show that the $Sr_2Ru_xIr_{1-x}O_4$ compounds

TABLE I. ^{99}Ru measurements in $Sr_2Ru_xIr_{1-x}O_4$.

	Sr_2RuO_4	$Sr_2Ru_{.7}Ir_{.3}O_4$	$Sr_2Ru_{0.5}Ir_{0.5}O_4$	Ru
Isomer shift (mm/s)	−0.25(0.01)	−0.24(0.01)	−0.30(0.01)	0(≪0.01)
Halfwidth (mm/s)	0.18(0.01)	0.17(0.01)	0.17(02)	0.16(<0.01)
d (mg/cm^2)	248(10)	200(10)	57(5)	500(10)

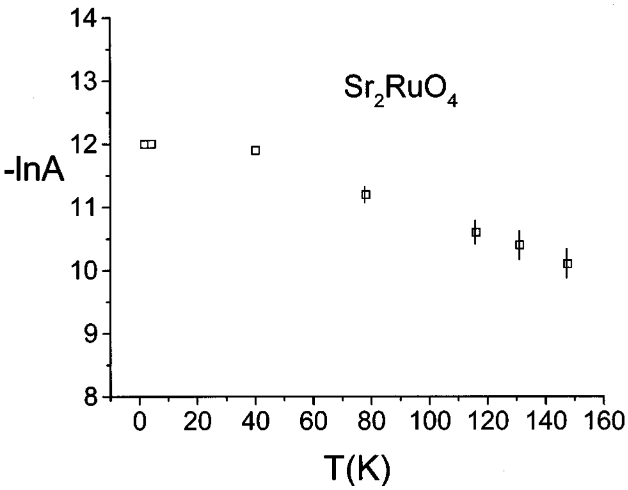

FIG. 5. The natural logarithm of the normalized (4.2 K) resonance area versus temperature for ME measurements of Sr_2RuO_4. The error bars represent the uncertainty in the area.

are consistent with a +4 ionization. The isomer shift is a combination of two independent multiplicative effects: the change of nuclear radius in going from the ground to the excited state (which is positive for ^{99}Ru) and the *s* electron density over the nuclear volume. Therefore, the isomer shift change of −0.05 mm/s shown in Table I (changing from $x=1$ to $x=0.5$) represents a decrease in the number of *s* electrons overlapping the nucleus. This can be explained two ways: (1) a decrease in the total number of *s* valence electrons and (2) an increase in the number of *d* electrons, which can shield *s* electrons from the nucleus.[15] The second explanation is plausible because more $5d$ electrons are becoming available as a result of Ir substitution into the solid solution. This may be the result of more electrons moving into the t_{2g} energy levels. This results in an ionization state for ruthenium being slightly less than +4. Similar arguments have been made for $3d$ electrons in iron, which are in the same column of the periodic table.

The change in the isomer shift measurement correlates with an increase in electron density in the conduction band due to the addition of *d* electrons as Ir is added to the solid solution. This would cause the Fermi energy to move to a higher energy. And, therefore, in the first approximation, the density of states would become larger. Then, if the *d* electron energy band were originally narrow, as some have argued,[1,16] than it would become even narrower with the addition of Ir. And, therefore, the possible nondegenerate energy level, d_{xy}, could develop an energy gap due to a small energy change giving rise to the metal insulator transition observed between $x=0.7$ and $x=0.5$.

The neutron diffraction measurements show that there is some structural change accompanying the change from Sr_2RuO_4 to Sr_2IrO_4 as was the case for $La_{2-x}Ba_xCuO_4$. But, the ^{99}Ru ME spectra for all compounds with $x \geqslant 0.5$ show a single unbroadened line and, therefore no measurable electric quadrupole interaction as displayed in Fig. 3 for RuO_2. The electric quadrupole interaction measures the electric field gradient across the nucleus caused by the crystalline environment. The ME measurements suggest that the oxygen octahedra surrounding the Ir-Ru are rigidly rotated about the *c* axis and therefore do not make any contribution to the electric field gradient, as is the case with RuO_2.[17] This is consistent with the neutron diffraction work which shows a rotation of the of the oxygen octahedra about the *c* axis.

There are many physical reasons to consider the spectrum measured for $Sr_2Ru_xIr_{1-x}O_4$. $x=0.4$ compound in Fig. 4 to be a magnetic spectrum. The first is that all the compounds from $x=1$ to $x=0.5$ exhibit single line spectrums and it would be unusual for system to develop a disordered state at $x=0.4$ and not before it. Therefore the broadened line probably does not represent a disordered multiple line state. Secondly, the neutron diffraction measurements suggest that the structural change between the $x=1$ and $x=0$ compounds represents a rigid rotation of the oxygen octahedra and therefore not a deformed structure. Thus rigid rotation would not result in an electric field gradient and a therefore a quadrupole interaction split spectrum. This is verified by the single narrow lines in the ME spectra for $x \geqslant 0.5$. Thirdly, the IS measurement at $x=0.4$ for the magnetic interaction is consistent with the $x=0.5$ measurement. Fourthly, there is a measurement of the iridium ME in Sr_2IrO_4 performed by Wagner.[18] In this measurement the hyperfine magnetic field at the Ir nucleus was determined to be 24 T with no quadrupole splitting. If one uses the ratio of the hyperfine coupling constants[19] for Ir/Ru, which is about 4, it is found that the hyperfine magnetic field at Ru should be about 6 T. This compares quite favorably with the ME measurement at Ru of 7.2(1.5) T.

The interpretation of the magnetic hyperfine field at the Ru nucleus for the $x=0.4$, $Sr_2Ru_xIr_{1-x}O_4$ compound, is that it has become magnetically ordered. The spin polarized *d* electrons produce a difference in the *s* electron spin density at the Ru nuclei via an electron spin interaction between *s* and *d* electrons. And, this results in a Fermi contact hyperfine magnetic field of 7.2(1.5) T. This small hyperfine magnetic field is consistent with a weak ferromagnet.

In conclusion, it was shown that there is an electronic change measured by the isomer shift change which occurs between $x=0.7$ and $x=0.5$ that is the signature of the MI transition. There is a magnetic phase transition at $x=0.4$ as evidenced by the magnetic hyperfine interaction. It is found that there is no measured distortion in the octahedral environment of ruthenium in all ME measurements. Therefore, it is still an open question about which mechanism (crystalline distortion and/or electronic correlation effects)[20] is responsible for these transitions in $Sr_2Ru_xIr_{1-x}O_4$. The ^{99}Ru ME has been measured over a large range in temperature in Sr_2RuO_4, with no observation of phonon nor isomer shift anomalies and the high temperature estimation of the Debye temperature has been obtained for Sr_2RuO_4. And, it has been demonstrated that the ^{99}Ru ME can be measured in the super-conducting state below 1.8 K where muon spin resonance measurements observe a magnetic field.[21]

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