GROWTH AND CHARACTERIZATION OF Sr_2RuO_4 AND Sr_2RhO_4

GROWTH AND CHARACTERIZATION OF $\rm Sr_2RuO_4$ AND $\rm Sr_2RhO_4$

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A Thesis Submitted to the School of Graduate Studies in Partial Fulfillment of the Requirements for the Degree Master of Science

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Abstract

We report on the growth and characterization of strontium ruthenate (214) (Sr_2RuO_4) and strontium rhodate (214) (Sr_2RhO_4) in efforts to test their agreement with Landau-Fermi liquid theory using optical measurements. We begin by reviewing the theory of Landau-Fermi liquids and the frequency and temperature dependent conductivities. We review existing work on both Sr_2RuO_4 and Sr_2RhO_4 including evidence of agreement with Landau-Fermi liquid theory. We also describe optical floating zone crystal growth and the exact procedures we used to prepare samples of both Sr_2RuO_4 and Sr_2RhO_4 via optical floating zone. The resulting Sr_2RuO_4 crystals were characterized using AC susceptibility measurements and Sr_2RhO_4 by powder diffraction, single crystal diffraction, and SQUID magnetization measurements. Finally, early optical reflectivity measurements at low temperatures are presented.

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Chapter 1

Introduction

Optical spectroscopy can be used to study a large variety of materials, at a wide range of temperatures, and with wide ranges of probing photon energies - from the ultraviolet to the far infrared. It can be used to study excitations such as optical phonons, magnons, band structure features, and energy gaps - and their evolution with temperature. As a more concrete example, it can be used to measure the changing size of the superconducting gap (in energy) with temperature below the superconducting transition temperature. See figure 2.4 for further examples.

These changes do not require sharp transitions or strange materials. In simple metals, at low temperatures, the electron scattering rate - which governs a material's resistivity ρ - should cease to be dominated by phonons, due to the complete 'freezing out' of phonons, and leave only electron-electron interactions. In the simplest picture, this results in a T^2 resistivity and is conventionally labeled '(Landau-)Fermi liquid' behavior. Since resistivity also governs a material's reflectivity, via its dielectric constants, this property can be observed optically.

However, as photons carry energy and can transfer it to electrons in much the same way as thermal energy, there are corresponding conditions on the frequency dependence ($\rho(\omega)$). This is explored in section 2.2.2. To date, no materials which exhibit T^2 resistivity have conclusively shown Landau-Fermi liquid-like behavior of $\rho(\omega, T)$, as shown by Nagel *et al.* [43]. It remains an open question as to whether Landau-Fermi liquid behavior is ever obeyed, except in the simplest of materials - which have such low energy regimes for phonon-freezing as to be inaccessible to all current optical measurements. This is mainly due to the difficulty in accessing the appropriate frequency regime.

In this thesis, we explore a material heralded as an exemplary Landau-Fermi liquid - strontium ruthenate (214) (Sr₂RuO₄). Although the T^2 resistivity in this material is well studied, the same cannot be said of its $\rho(\omega)$ behavior, as will be detailed in chapter 3. We do not intend to dispute the previous studies on T^2 behavior, or the agreement observed between measurement techniques such as ARPES and quantum oscillations, but rather to better explore $\rho(\omega)$, so as to be able to make arguments as to the agreement with Landau-Fermi liquid theory. We also make note of the need for caution in light of its anisotropy and high effective masses. However, before measuring $\rho(\omega)$, it will be extremely important characterize our material's purity and structure.

We also study a sister compound - strontium rhodate (214) (Sr₂RhO₄). Although the chemical formula is very similar, it doesn't superconduct, while Sr₂RuO₄ does. While $\rho \propto T^2$ has been previously shown, to the best of our knowledge $\rho(\omega)$ measurements at appropriate temperatures have not been done. See the discussion of optical measurements contained in section 3.3. We hope to make the first such measurements on this material. If we can identify differences in this behavior between the two, given their well understand electronic structure, we may be able to make an argument as to why - and provide insights as to how to verify - or dispute - Landau-Fermi liquid theory in the future.

1.1 Structure of thesis

This thesis consists of 7 chapters, as well as 3 chapters in the appendix. Chapter 2 elaborates on the theory and experimental background and techniques necessary to understand the remainder of the thesis. Chapter 3 reviews previous work on these materials, and more strongly supports some of the arguments made in the introduction. In chapter 4 the procedures used to grow the materials used in this thesis are detailed - although more complete instructions are contained in appendix A. The results of the characterizations of these materials are contained in chapter 5. The results of the optical measurements are contained in chapter 6. Finally, we discuss the net results of this study and conclude the thesis in chapter 7. Crystal growth step-by-step instructions, the results of single crystal refinement, and MATLAB code used in the thesis are contained in the appendix. Though already discussed in the acknowledgments, significant contributions by others are noted in their respective sections.

Chapter 2

Theory

2.1 Introduction

This chapter will cover the key elements of theory necessary to understand and interpret subsequent results, along with brief explanations of the equipment used to obtain those results and the analytical techniques and equations used, if appropriate. First, theories of resistivity at low temperature will be discussed, followed by resistivity measurements - first DC, then optical - and finally x-ray and magnetic measurements.

2.2 Resistances of metals at low temperatures

At low temperatures, the resistivity of pure metals changes dramatically. The exact behavior depends on the temperature range, the material, and occasionally other factors. The conductivity σ can be described in most materials using the extended Drude model:

$$\sigma(\omega, T) = \frac{1}{4\pi} \frac{\omega_p^2}{(1/\tau(\omega, T)) - i\omega(1 + \lambda(\omega, T))}$$
(2.2.1)

where τ is the scattering rate, λ the mass enhancement of the charge carriers, and ω_p is the plasma frequency of the material, all of which are in general not known - although they can be extracted from optical measurements. This describes a general system in which charge carriers are scattered by bosons. However, we know what ρ behaves like in some special cases. The temperature dependence of resistivity is more commonly studied, due to its accessibility in DC resistivity measurements, and so it is the first topic explored here [2].

2.2.1 Temperature dependence of resistivity

Landau showed that when electrons are allowed to interact with each other, a result emerges now known as Landau-Fermi liquid theory. In some cases, the name is shortened to simply "Fermi liquid theory". The essence of the theory is that, upon starting from the independent electron approximation - that is, the Fermi gas - electron-electron interactions can continuously be 'turned on' to generate a set of fermionic charge carriers from the original electrons. The electron-electron interactions typically take the form of electrostatic repulsion resulting in electron-electron scattering. Due to the Pauli exclusion principle, the scattering rate is much lower than might be expected. This requires Umklapp processes (processes which do not conserve momentum but do conserve crystal momentum) to contribute in order to actually degrade the electron transport. Upon considering how thermal excitations from absolute zero affect the occupation of electrons within - and near - the Fermi surface, a resistivity proportional to T^2 can be derived [1, Chap. 17].

Phonons, oscillations in the underlying atomic lattice, can also scatter electrons. After properly accounting for the available phonons and electrons at low temperatures, as well as the reduction in the efficiency of the scattering to increase resistance - as Umklapp processes become increasingly energetically unfavorable at low temperatures - it is possible to derive the effect of phononelectron scattering on resistivity: $\rho \propto T^5$. This is known as the Bloch T^5 law. At higher temperatures - temperatures above the Debye temperature - it results in $\rho \propto T$ [1, Chap. 26].

For materials containing dilute magnetic impurities - for example, a small fraction of iron atoms scattered amongst a large crystal of some other material - a phenomenon known as the Kondo effect emerges. This causes the conduction electrons to become spin polarized around the impurities to magnetically screen them. This results in an upturn in resistivity at very low temperatures proportional to $-\ln(T)$ [6, Chap. 7.10].

2.2.2 Frequency dependence of resistivity

A frequency dependent resistivity ρ can be extracted from Landau-Fermi liquid theory, as was first done by Gurzhi [16]:

$$\rho(\omega, T) = A((\hbar\omega)^2 + 4(\pi k_B T)^2).$$
(2.2.2)

Both the frequency and temperature dependence of the resistivity appear only as squares, and the ratio between temperature and frequency scaling terms should be $4(\pi k_B)^2/\hbar^2$.

More careful analysis of the theory by Maslov and Chubukov [40] revealed a somewhat more general scaling law at a wider range of frequencies:

$$\rho(\omega, T) = A((\hbar\omega)^2 + b(\pi k_B T)^2) \qquad (2.2.3)$$

- with $b \approx 4$. This requires Umklapp processes to occur for finite resistivity at $\omega = 0$ - that is, for DC resistivity measurements, but both Umklapp and normal processes were considered in deriving the result. From now on, if *b* is referred to, it is the *b* in equation 2.2.3 we are referring to. Note that *A* is positive in equations 2.2.2 and 2.2.3.

Maslov and Chubukov [40], as part of their work, expanded on the Kondo resistivity discussed earlier, using the Wilson ratio - a ratio of the absolute zero magnetic susceptibility and the linear coefficient in specific heat - to derive a frequency dependent resistivity in low orders of T and ω :

$$\rho = B - C((\hbar\omega)^2 + 2(\pi k_B T)^2). \qquad (2.2.4)$$

with both B and C positive, and so materials in the Kondo regime - sometimes called Kondo Fermi liquids - obey a similar scaling to that shown in equation 2.2.3, but with increasing frequency the resistivity decreases, and the 'effective b' is 2.

This led to a general insight that, according to Maslov and Chubukov [40], b in equation 2.2.3 can effectively be a measure of the relative contributions of elastic and inelastic scattering to the resistivity. Electron-electron scattering is inelastic for Landau-Fermi liquids, so elastic scattering arises from some alternative source. A value of b = 1 indicates scattering dominated by resonant elastic mechanisms - that is, mechanisms with no frequency dependent scattering.

(b) 4 - Lead Arrangement



Figure 2.1: Figure 7.2b of Ekin [13], reproduced with permission. A four-point probe resistance measurement setup on an ideal bar-like sample. Note the two voltage and two current probes.

One such source of elastic scattering is the scattering from a resonant energy level - either one from an impurity, or one intrinsic to the material - for example, highly localized f electrons [40]. To date, most materials that have been measured do not have b = 4 [43].

2.3 DC resistivity measurements

A common geometry used in DC resistivity measurements is the 4-point probe technique shown in figure 2.1. By separating the current and voltage contacts, the resistance due to the wiring and the sample contacts can be eliminated. However, the distance between voltage contacts as well as the cross sectional area must be measured to obtain accurate results. This also means regular, bar-like samples are the easiest to work with.

Another common geometry is known as Van der Pauw, and is demonstrated in figure 2.2. Each of the 4 contacts in the Van der Pauw method are used as both voltage and current contacts. By comparing the various measured resistances as the contact roles vary, the exact resistivity - independent of the sample geometry, except its thickness d and a requirement of being free of



Figure 2.2: Figure A7.2 of Ekin [13], reproduced with permission. Various sample shapes - and contact locations - for Van der Pauw measurements. The electronics hardware is otherwise very similar to figure 2.1 but with the capability to switch functionality of each contact on the fly.

holes - can be obtained. This means Van der Pauw measurements require less measurements of size, and the sample does not need to be bar-like [13, 60]. If we use any of the samples shown in figure 2.2, then the resistivity is:

$$\rho = \frac{\pi d}{2ln(2)} \left(R_{AB,CD} + R_{BC,DA} \right) f\left(\frac{R_{AB,CD}}{R_{BC,DA}} \right)$$
(2.3.1)

with $R_{AB,CD}$ the resistance measured using the voltage difference $V_D - V_C$ divided by the current entering contact A and leaving contact B, and f, a known function as shown in figure 2.3 [13, Pg. 595]. Additional details can be found in the MSc thesis of Mahsa Rahimi of McMaster University.

2.4 Reflection spectroscopy

The standard technique used in the Timusk lab at McMaster university is reflection spectroscopy. It involves measuring the power of reflected light and its spectral behavior resulting from its interaction with a sample. Since a spectrum is simply data over a range of frequencies, this automatically implies retrieving frequency dependent data from results. Usually this is done by comparing the amplitude of the initial light's electric field to the amplitude of the electric field of the light reflected from the sample. To extract complex quantities,



Figure 2.3: Figure A7.3 of Ekin [13], reproduced with permission, demonstrating the values of f, used in equation 2.3.1.

such as resistivity, the phase must be obtained from the amplitude using the Kramers-Kronig relations, as will be described and demonstrated later.

Reflection spectroscopy in its simplest form involves reflecting a monochromatic light beam off a sample and measuring the change in intensity in the beam between when it reflects off the sample, and comparing that result to when it reflects off a perfect, or known, mirror. Our version of spectroscopy uses a broadband source and a Fourier spectrometer to measure many frequencies of light simultaneously and Fourier transforms the resulting interferogram to obtain intensity as a function frequency. Depending on the wavelength, different interesting features may be observed - that correspond to the energy scale of the feature, as shown in 2.4 [2].

2.4.1 Setup and technique

All reflection spectroscopic measurements presented in this work were recorded using the lab's Bruker IFS 66v/S (referred to as 'Bruker' from here on) spectrometer, which can be outfitted with 4 different light sources to obtain a wide range of frequencies, and uses 4 different detectors to collect all of the



Figure 2.4: A demonstration of the energy and wavelength ranges that can be probed through optical spectroscopy, along with material-dependent features and their typical energy scales. Reprinted figure with permission from Basov and Timusk [2]. Copyright 2005 by the American Physical Society.

frequencies. This results in 5 'regimes' of study for our measurements, shown in table 2.1, though we tend to focus on the furthest possible infrared results most of the time, since it usually contains the most interesting information – e.g. effects that depend strongly on both temperature and photon energy, such as the Landau-Fermi liquid effects we are most interested in.

The core of the Bruker is a rapidly scanning Michelson interferometer. This allows an interference pattern - interferogram - to be taken rapidly, and thus a power spectrum (after Fourier transformation) to be measured at a similar rate. Since these power spectra contain information about a wide range of frequencies, we obtain frequency dependent power data from them. By comparing the measured power reflected from a sample to that from a known reference with the same size, an absolute reflectivity can be obtained.

With a monochromatic source, a Michelson interferometer modulates the intensity of the light depending on the path difference between two 'arms' of an optical path, due to interference between the electric fields, upon recombining those two arms - giving rise to a sinusoidal intensity as a function of path difference. For a continuous broadband source, each frequency present gives rise to a sinusoidal intensity variation with a different periodicity. This gives rise to

Frequency range	Detector	Light	BS	Window
Very far IR	1 K bolometer	Hg arc	$50 \ \mu m$	PP
$(10 - 200 \text{ cm}^{-1})$			mylar	
Far IR	4 K bolometer	Hg arc	Ge coated	PP
$(50 - 600 \text{ cm}^{-1})$		or globar	6 µm mylar	
Mid IR	MCT detector	Globar	KBr	KBr
$(400 - 6000 \text{ cm}^{-1})$				
Near IR	MCT detector	Tungsten	CaF_2	KBr
$(3000 - 14000 \text{ cm}^{-1})$		lamp		
NIR, Vis, UV	\mathbf{PMT}	Deuterium	CaF_2	KBr
$(12000 - 45000 \text{ cm}^{-1})$		lamp		

Table 2.1: The various operating regimes of the Bruker. MCT is shorthand for mercury-cadmium-telluride. PMT is shorthand for photomultiplier tube. BS is shorthand for beam splitter. PP is shorthand for polypropylene

a sinc-like total intensity as a function of path length. This interferogram can be Fourier transformed to give information about every frequency's intensity.

The Bruker contains other optical elements, shown schematically in figure 2.5 [64], mainly to guide the beam onto the samples, but also to control the size of the beam, for a technique called 'overfilling'. In this technique, the beam of light used to probe a sample is chosen to be larger than the sample itself. This allows irregular samples to be more easily measured. In exchange, the sample mounts must be designed so as to scatter light that does not fall on the samples away from the detector. The samples mounts can be seen in figure 2.6 [21].

One final element, not shown in figure 2.5 because it is directly below element N, is the gold evaporation compartment. Although during measurements a piece of gold is used as a reference, if the ratio of power between a sample and that gold reference were taken, the magnitude would depend on the ratio of their sizes, as well as differences in surface roughness and associated scattering. By evaporating a thin layer of gold onto the sample, this size and surface effect can be corrected for, using equation 2.4.1.

$$R_{\text{abs, sample}} = \frac{P_{\text{sample}}}{P_{\text{gold reference}}} \frac{P_{\text{gold reference}}}{P_{\text{sample+evaporated gold}}} R_{\text{abs, gold}}$$
(2.4.1)

Detectors are usually cooled for data collection. For some detectors, such as bolometers, this results in the detector's resistance becoming very sensitive to incident energy - due to thermal heating - and thus providing a heat-based



Figure 2.5: A top-down schematic of the optical components of the Bruker 66 v/s. A is the light source. C is a pinhole that controls the diameter of the beam. F is a beamsplitter. E, F, and H form the Michelson interferometer. L1 and L2 control the alignment onto the sample and the detector, respectfully. N is the sample on the cryostat inside its vacuum chamber. O is the detector. Adapted from Yang [64].



Figure 2.6: Two brass sample holders used in the Bruker 66 v/s. The circular flat portion is used to support the sample, and its size is modified depending on the size of the sample. The rest of the mount is sloped to scatter away excess light. 6 screw holes are visible here, 2 of which are threaded. These are used to align the sample.

measure of power. For other detectors, such as the mercury-cadmium-telluride (MCT) detector, cooling is necessary to prevent thermal excitation of carriers across a band gap. Detectors are cooled to temperatures as low as ≈ 1.2 K. Other detectors, such as photomultiplier tubes, require no cooling at all, but are only sensitive to higher energy photons (those further towards the visible). In general, the less far into the infrared, the less cold the detector needs to be.

Because of our operation in the far infrared, both the interior of the Bruker and the sample chamber need to be evacuated. This is to reduce the effect of absorption of common constituents of the air (e.g. CO_2 or water vapor) and to prevent ice formation. During data collection, users often check for the signs of ice build-up (typically via the strong absorption line corresponding to the O-H stretch near 3300 cm⁻¹) or changes in absorption that might indicate leaks or changes in pressure.

Even with these precautions in place, the rate of data collection is often low. Many dozens or hundreds of scans are collected for each final spectrum, which is formed from their average, reducing the noise. A single measurement (after averaging) of the power spectra of a single sample typically takes more than 8 minutes.

2.4.2 Data analysis and theory

Note that in this section, the equations are written in CGS units, as opposed to the more commonly used SI units. Therefore, for example, ω is in units of cm⁻¹. This system of units will also be used in further discussions of optics, for example in chapter 6.

The collected data are taken in the form of an interferogram. This contains information on the power as a function of path difference - that is, in wavelength space. A Fourier transform of this data converts it into frequency space, yielding a power spectrum. These power spectra are what is usually analyzed and saved. After measuring the sample and the reference - both before and after evaporating gold on the sample - we use equation 2.4.1 to obtain the reflectance.

The reflectance of a sample is related to its index of refraction. However, to obtain full information on the index of refraction - which is a complex quantity - one must also obtain information on the phase shift caused by reflection. One way of finding the phase shift is based on a mathematical theorem borrowed from complex analysis - the Kramers-Kronig relation:

Assuming the response function α to a sinusoidal field is passive and linear

For
$$\alpha(\omega) = \alpha_1(\omega) + i\alpha_2(\omega)$$

with $\operatorname{im}(\alpha_1(\omega)) = \operatorname{im}(\alpha_2(\omega)) = 0 \forall \omega$
 $\alpha_1(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{s\alpha_2(s)}{s^2 - \omega^2} ds$
 $\alpha_2(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{\alpha_1(s)}{s^2 - \omega^2} ds$
(2.4.2)

which can be applied to causal data (with some conditions) to obtain the complex part. This means it applies to most - but potentially not all - optical systems.

The Kramers-Kronig relation can be viewed as developing from Cauchy's residue theorem in complex analysis, which involves the integral of a complex function. The function can be split into real and imaginary parts to create a linkage between them. The general conditions on its applicability are the same as stating that a response function must be causal - that is, not depend on conditions from the 'future'. A set of reflectivity data - obtained by taking the ratio of electric fields incident on and reflected from a sample - is a response function - the complex reflectance r. It is intuitively causal as you cannot obtain a reflection from a sample before light interacts with a sample. We describe the exact restraints in more detail below.

There are several conditions on use of the Kramers-Kronig relation, which can be described in four points. First, the system's response function must be linear. This means that if the system is nonlinear - for example, materials with nonlinear polarizability - the equations may not apply. With low intensity light, almost all systems can be approximated as linear. Second, the response function must be passive, or causal. This is a specific case in which the poles of the complex function all have negative or zero imaginary components. In a real system this can be viewed as the relaxation frequencies of the system being positive. This rules out active mediums, such as laser gain mediums. Third, the response function must go to zero uniformly as the frequency approaches infinity. Systems can become nearly transparent to very high frequency photons (e.g. gamma rays) so this seems reasonable. Finally the system needs some symmetry about $\omega = 0$, but negative ω is meaningless so this is permitted [28]. The issue with this is that it requires data out to both zero frequency and infinite frequency. The zero frequency data can be obtained from DC resistivity measurements, but the regimes between zero frequency and the lower bound of our measurements, as well as the upper bound of our measurements and infinite frequency, are difficult to obtain. After combining all experimental data, physically reasonable extrapolations are made to both zero and infinite frequency, as discussed later, to generate the data used in the Kramers-Kronig relation.

The reflectivity R gives us the magnitude of the reflection coefficient r:

$$r = \sqrt{R} \exp^{i\theta}$$

$$\ln(r) = \frac{1}{2} \ln(R) + i\theta$$
(2.4.3)

We can then combine equation 2.4.3 with equation 2.4.2 to obtain the phase θ as shown in equation 2.4.4.

$$\theta(\omega) = \frac{\omega}{\pi} \int_0^\infty \frac{\ln(R(\omega')) - \ln(R(\omega))}{\omega^2 - \omega'^2} d\omega'$$
(2.4.4)

From these, the complex index of refraction $N = n + i\kappa$ of a sample can be calculated, which yields the remaining electromagnetic properties of the material - including the conductivity, as shown in equation 2.4.5 [64].

$$n = \frac{1 - R}{1 + R - 2\sqrt{R}\cos(\theta)}$$

$$\kappa = \frac{-2\sqrt{R}\sin(\theta)}{1 + R - 2\sqrt{R}\cos(\theta)}$$

$$\epsilon_1 = n^2 + \kappa^2 \qquad (2.4.5)$$

$$\epsilon_2 = 2n\kappa$$

$$\sigma_1 = \frac{\epsilon_2\omega}{4\pi}$$

$$\sigma_2 = \frac{\omega}{4\pi}(1 - \epsilon_1)$$

Most of this analysis is performed in a single step using MATLAB programs created by each individual member of the group. However, Prof. David Tanner of the University of Florida provides a large number of optical analysis programs for free on his webpage which have been used in some cases to verify the accuracy of data. One of Prof. Tanner's programs also automatically generates $K-\alpha$ and $L-\alpha$ x-ray absorption data based on chemical formula, which is used for the high frequency extension. Users still need to generate the x-ray spectrum - or obtain x-ray data from other sources - and splice the various datasets together manually.

As for the low frequency extension, DC resistivity data is usually used to provide the value at $\omega = 0$, with an approximation function connecting the lower bound of the optical data to it. For insulators, usually the reflectance is assumed to be constant to zero frequency. For metals, the Hagen-Rubens relation is generally used:

$$R = 1 - A\sqrt{\omega}.\tag{2.4.6}$$

for A a positive constant. For superconducting materials a different extrapolation is used, however, this is beyond the focus of this work [64].

2.5 Spectroscopic ellipsometry

Spectroscopic ellipsometry can be thought of as a special case of reflection spectroscopy. The key difference is that ellipsometry measures the change in polarization of light after interaction with a sample instead of the amplitude of the light's electric field after interaction with a sample, as in the case of reflection spectroscopy. A broadband light source and polarizing elements are used to determine the change in polarization as a function of frequency. However, ellipsometry is performed at oblique - not normal - incidence, in order to differentiate between s and p polarized light. This complicates the analysis somewhat.

An ellipsometer will measure the values ψ and Δ , which are the amplitude ratio and phase difference between s and p polarized light, respectively. These need to be converted into the complex refractive index N, which is non-trivial for thin samples, due to the multiple interfaces of reflection and refraction. In a particularly simple case, with only the air-sample interface and the underside of the sample contributing, and an incident angle of θ_0 , the complex index of refraction N can be calculated as:

$$\tan(\psi)\exp(i\Delta) = \frac{\frac{N\cos(\theta_0) - \cos(\theta_1)}{N\cos(\theta_0) + \cos(\theta_1)}}{\frac{\cos(\theta_0) - N\cos(\theta_1)}{\cos(\theta_0) + N\cos(\theta_1)}}$$
(2.5.1)

with θ_1 the angle of light inside the sample [15]. In more complex cases, an optical model needs to be constructed in order to extract relevant quantities.

For anisotropic materials, the situation is considerably more complicated, as each possible orientation has an associated index of refraction. In order to obtain quantitatively correct measurements, it is necessary to perform more rigorous measurements - for example, rotating the sample or light source over multiple measurements in order to determine the orientation dependence of the material. This results in significantly more complicated analysis. However, in certain particular arrangements, shown in section 6.1.4 of Fujiwara [15], the situation can be somewhat simplified. These occur for situations where, if the s and p polarization directions are projected onto the sample face, they lie directly along a principle axis of the material.

2.6 X-ray diffraction

All x-ray diffraction experiments can be viewed as special cases of the Bragg formulation, which indicates that when planes in a crystal are separated by a distance d and probed by x-rays of wavelength λ , we obtain constructive interference as a function of angle θ when the condition:

$$n\lambda = 2dsin(\theta) \tag{2.6.1}$$

is satisfied for integer n. This is equivalent to saying that constructive interference occurs when the difference between an incident and scattered x-ray's wave vector, K, is a reciprocal lattice vector [1, Chap. 6].

Constructive interference at discrete locations requires a regular lattice with an associated regular reciprocal lattice. If a lattice is highly disordered, the inter-plane distance d will vary - as will the reciprocal lattice vectors. Therefore x-ray diffraction can be used to measure the crystalline nature of a sample.

One way to visualize this is using the Ewald construction. The incident wave vector is drawn from the origin of the reciprocal lattice, and then a sphere in k-space is drawn around its tip, with radius equal to the magnitude of the incident wave vector. Constructive interference only occurs when another reciprocal lattice point lies on the edge of the sphere. This can be seen in figure 2.7. The various types of diffraction measurements can be seen as various



Figure 2.7: The Ewald construction, adapted from Figure 6.7 of Ashcroft and Mermin [1]. The dots indicate reciprocal lattice points. The incident and scattered x-ray wave vectors are labeled by k (in red) and k' (in blue), respectively. The sphere is of radius k. This shows the condition for constructive interference from the reciprocal lattice point k' which is at $k_x = 3$ and $k_y = -1$.

ways of manipulating the sphere in k-space [1, Chap. 6].

2.6.1 Laue diffraction

Laue diffraction is performed with the crystal fixed in space but a continuous spectrum of x-ray wavelengths are used to probe the material instead. This results in a continuum of nesting Ewald-constructed spheres in k-space, for example as shown in figure 2.8. Then constructive interference occurs for all reciprocal lattice points contained within the continuum. As the crystal is fixed - and thus the orientation of the reciprocal lattice is also fixed - this allows the orientation of the reciprocal lattice to be measured, and thus the orientation of the real crystal as well.

Usually the scattered x-rays are captured on a 2-d camera, which, when the pixel spacing of the camera and the distance from the camera to the sample are both known, allows the measurement of constructive diffraction spots with angle, which allows the scattered wave vector to be determined. From this, the reciprocal wave vector is obtained, and a measurement of the real space lattice is then possible. In many Laue diffractometers, software is used to generate



Figure 2.8: The Ewald construction can be used to visualize Laue diffraction experiments, as shown in this reproduction of Figure 6.8 of Ashcroft and Mermin [1]. Due to the spread of x-ray wavelengths, the incident wavevector varies from a min k (in red) to a max k (in blue), and thus creates a continuum of nested spheres - the purple shaded region. Inside this shaded region, all reciprocal lattice points (the dots) generate constructive interference.

a scattering pattern from theoretical crystal structures, and then compared to the measured one. This allows a qualitative measurement of the crystal structure as well as a determination of its orientation.

2.6.2 Single crystal diffraction

Single crystal diffraction uses a fixed, monochromatic x-ray source, and a single crystal of the sample is slowly rotated. As the crystal is rotated, a 2-d camera takes images of the scattered x-rays, thus mapping the effect of the rotation on the constructive x-ray scattering. [1, Chap. 6]

This can be visualized using the Ewald construction as the reciprocal lattice slowly rotating as the incident x-ray Ewald sphere stays fixed. Constructive interference occurs whenever the reciprocal lattice is rotated such that a point on the lattice intersects the edge of the Ewald sphere. This is demonstrated in figure 2.9.

Single crystal diffraction results in many large 2-d images of diffraction spots. Software is then used to compile the spots together into a 3-d diffraction pattern. This involves merging the images together, locating spots, and measuring their periodicity. During this step, the lattice and lattice parameters of a crystal are obtained. Once the crystal lattice is known, the diffraction pattern peaks are associated with specific reciprocal lattice vectors. These intensities as a function of reciprocal lattice vector help reveal the crystal structure, which can be refined using programs such as Olex2 to determine atomic occupancies, anisotropy of atoms, and the likelihood of impurities.

2.6.3 Powder diffraction

Powder diffraction uses powder samples, and thus has a uniformly random orientation of the real and reciprocal lattices. It can be viewed as an extension of single crystal diffraction, except instead of the sample rotating, the sample is powdered and thus has a uniform distribution of all possible orientations. The intensity of the scattering is measured as a function of the scattering angle, which depends on the specific reciprocal lattice being probed, but independent of that lattice's orientation. This allows the composition of a small sample to be determined - and the average composition of a large batch of powder to be similarly determined [1, Chap.6].



Figure 2.9: The reciprocal lattice (the dark spots) is rotated with the crystal, while the incident x-ray direction and wave vector k (in red) are fixed, resulting in a series of intersecting 'orbits' (in grey) with the Ewald sphere. Any time the crystal is rotated such that a reciprocal lattice point along an orbit intersects the Ewald sphere's edge, a diffraction spot with wave vector k'will appear. This figure is adapted from figure 6.9 of Ashcroft and Mermin [1].

This can be visualized in the Ewald construction as having a fixed input x-ray of fixed wave vector k, but having the reciprocal lattice rotated in all possible angles about the origin. Constructive interference is only observed at scattering angles $\phi(=2\theta)$ when K,

$$K = 2ksin(\frac{1}{2}\phi) = 2ksin(\theta)$$
(2.6.2)

is a reciprocal lattice vector [1, Chap.6].

Powder diffractometers return intensities as a function of 2θ . Using equation 2.6.2, the reciprocal lattice can be determined, and thus the real space lattice. Usually the resulting data is compared to previously measured data to determine agreements or disagreements, for example using the Inorganic Crystal Structure Database or the International Centre for Diffraction Data's PDF databases.

A question that needs to be asked when interpreting powder x-ray results is "Do these results meaningfully reflect the samples I will use later?" It is not always obvious what the answer is, as it depends strongly on how you handle, isolate, and prepare materials for sample use and for powder x-ray. If you are biased in your selection - e.g. only taking materials from the edge of the growth for powder but using the center for your samples, you cannot necessarily trust your powder x-ray results as being relevant to your subsequent measurements.

2.7 AC susceptibility

AC susceptibility is measured using an AC susceptometer, which can be thought of two nested solenoids. Inside a solenoid, a nearly-uniform magnetic field can be generated by driving current through it. Thus, if a crystal is suspended inside a solenoid, it can be subjected to a uniform - and thus simple magnetic field. If the sample has its own magnetic response, the magnetic field inside the solenoid will be modified. By using a second solenoid - the pickup coil - wrapped around the first, this modified magnetic field can be measured using the induced current and thus voltage. Usually two oppositely wound, spatially separated coils, made from a single wire, are used as the pickup coil, which eliminates the mutual inductance between the pickup and driving coil and leaving only the response from the sample. By measuring the applied
magnetic field, the susceptibility χ , defined as:

$$\chi = \frac{\partial M}{\partial H} = \frac{\partial (\text{Magnetization})}{\partial (\text{Applied field})}$$
(2.7.1)

can be measured [44]. A typical AC susceptometer is shown in figure 2.10, as well as a photograph of the pickup and driving solenoids used in Kyoto University shown in figure 2.11.

If the applied current is varied at a fixed frequency, the response function will have a component that oscillates at the same frequency, corresponding to the pickup coil's response to the magnetic field. Thus a lock-in technique can be used to eliminate extra signals and also measure the phase of the response, by using the real and imaginary results of the lock-in amplification.

If the sample can be suspended on a thermally-controlled material - e.g. strips of wires or a solid rod - the magnetization and susceptibility can be measured as a function of temperature, thus allowing magnetic phase transitions to be identified. If the sample is a superconductor, which exhibits perfect diamagnetism, the real part of the amplified signal will suddenly drop to a constant negative value. At Kyoto University, the sample is suspended on metal wires within the coils shown in figure 2.11 to control the temperature.

2.8 SQUID magnetization

A superconducting quantum interference device (SQUID) can be used to measure the magnetization response of a sample by making use of the Josephson tunneling effect - in which superconducting Cooper pairs can tunnel across non-superconducting regions. This create a measurable voltage loss in a loop of superconducting wire with a small section of non-superconducting material [6]. As magnetic flux is introduced, so are screening currents in the superconductor, which modify the voltage response of the system. This allows the quantity of the magnetic flux passing through the superconducting ring to be measured [14].



Figure 2.10: Figure 7 from Nikolo [44] demonstrating the setup of an AC susceptometer for low temperature measurements. Note the sample positions, the primary and secondary coils. Though not shown, the two secondary coils are connected and wound in opposite directions, cancelling out the response from the primary coil. Reproduced with permission from Nikolo [44], copyright 1995 American Association of Physics Teachers.



Figure 2.11: A photograph showing the three pickup and driving solenoids for measuring AC susceptibility used at Kyoto University. These allows measurements of three samples in a single run. Samples are mounted on strips of wire suspended inside the solenoids (not shown).

Chapter 3

Previous work

3.1 Introduction

This chapter provides an overview of the known relevant material properties (in particular those measured via the techniques discussed in chapter 2) for strontium ruthenate (214) (Sr_2RuO_4) and strontium rhodate (214) (Sr_2RhO_4). A special focus will be given to existing optical measurements of these materials, in order to both contextualize and justify this work.

3.2 Overview of past Sr_2RuO_4 work

Although Sr_2RuO_4 was studied since at least 1959 [49], it was not until 1994 that Dr. Yoshiteru Maeno and others, at Hiroshima University, discovered superconducting behavior below 1.5 K in a Sr_2RuO_4 crystal grown by optical floating zone techniques. It garnered additional interest due to being isostructural to another unconventional superconductor known as LBCO $(La_{2-x}Ba_xCuO_4)$ while lacking copper in its structure, a common feature of most other unconventional superconductors at that time [35]. Suggestions of *p*-wave superconducting symmetry - which is beyond the scope of this work also spurred research, as described by Mackenzie and Maeno [31], for example.

After the discovery of superconductivity, subsequent work from the same group identified T^2 resistivity behavior below 25 K - for example as shown in figure 3.1 and as described by, for example, Maeno and Yoshida [37]. The behavior is strongly anisotropic, as first observed by Lichtenberg *et al.* [29].



Figure 3.1: The resistivity of Sr_2RuO_4 along both the *ab*-plane and the *c*-axis as a function of T². The *c*-axis resistivity is on the order of 100 times larger than that of the ab-plane. Reproduced with permission from Maeno *et al.* [38]. Copyrighted by the Physical Society of Japan.

Various other measurements of its electronic structure have been performed, yielding exceptionally good knowledge of its Fermi surface, and is supported by many different experimental techniques, for example in Shen *et al.* [53]. A substantial review of Sr_2RuO_4 is contained in Bergemann *et al.* [4].

Much work has been performed on analyzing the unconventional superconductivity of the material. However, in this study we primarily focus on the non-superconducting regime and thus are not particularly interested in the precise mechanisms of superconductivity. However, for those curious, discussions of the superconductivity are available, for example from Mackenzie and Maeno [31].

One common problem with the growth of Sr_2RuO_4 is that, due to the initial overdoping of ruthenium, the final material is eutectic with ruthenium metal - containing small inclusions of pure ruthenium. This has been termed the 3 K phase, due to the improved superconductivity beginning at 3 K. The theoretical implications of this have been explored by, for example, Sigrist and Monien [55] and Kaneyasu *et al.* [23], along with experimental measurements in papers such as Kittaka *et al.* [27] and Maeno *et al.* [36]. One explanation is that the inclusions cause an internal pressure effect, increasing T_c [19]. An additional common eutectic impurity phase is that of Sr₃Ru₂O₇, which has been studied by, for example, Kittaka *et al.* [26]. An example of the effects of the 3 K phase are shown in figure 3.2.

3.2.1 Katsufuji et al.

In 1996, Katsufuji *et al.* [24] prepared samples of Sr_2RuO_4 by the optical floating zone growth technique, independently of the ongoing research centered around Dr. Yoshiteru Maeno and colleagues. Traditional reflection spectroscopic measurements of a single sample were made from $\approx 64 \text{ cm}^{-1}$ to $\approx 50000 \text{ cm}^{-1}$, and using synchrotron radiation for even higher photon energies. Data was presented at temperatures of 9, 15, 60, 130, 200, and 290 K along both the *a* and *c* axes of the crystal, using polarized light.

These measurements are of limited use for our purposes for several reasons. First, only two data points are shown within the Fermi liquid temperature regime, and so do not reveal enough information about the temperature dependence of the resistivity. Secondly, if we make a naive assumption as to the frequency range where Fermi liquid-like scaling would apply, we obtain a maximum frequency of $\approx 100 \text{ cm}^{-1}$, and so a very small number of frequency points within the Fermi liquid regime were obtained as well. This is corroborated by their own admission that ω^2 is not observable. These two factors combined show that nothing can be obtained about the Fermi liquid scaling from these results.

Finally, no measurements or discussions of sample purity are present within the paper - not even residual resistivity - and superconductivity was never measured. Therefore the quality of the Sr_2RuO_4 sample measured within is completely unknown. Later measurements on the same sample (from Hildebrand *et al.* [20]) confirmed superconductivity, but at temperatures consistent with the 3 K phase.

However, within the paper, some discussions of features such as phonons - observed at 202, 363 and 484 cm⁻¹ - are present, which can be useful in judging our own data. These agreed qualitatively with optical phonons reported in Braden *et al.* [7], measured by inelastic neutron scattering.



Figure 3.2: Figure 2 from Maeno *et al.* [36], demonstrating the differences in the real part of the AC magnetic susceptibility (top), imaginary part of the AC magnetic susceptibility (middle), and the DC resistivity of Sr_2RuO_4 with (large symbols) and without (small symbols) small domains of ruthenium metal inclusions - the 3 K phase impurity. Note the broadness of the peaks and the early onset of diamagnetism. Reprinted figure with permission from

Maeno et al. [36]. Copyright 1998 by the American Physical Society.

3.2.2 Hildebrand *et al.*

In collaboration with Katsufuji and Tokura of the previous subsection, Hildebrand *et al.* [20] performed reflection spectroscopy measurements on a sample of Sr_2RuO_4 . It is stated to be the same crystal as in Katsufuji *et al.* [24]. Measurements were taken on the *c* axis at temperatures from 0.4 K to ≈ 90 K and from ≈ 10 cm⁻¹ to ≈ 6000 cm⁻¹, though only low frequency data are shown.

Hildebrand *et al.* [20] report the superconducting transition began at ≈ 3 K, indicating the strong presence of the 3 K phase. Furthermore the measured residual resistivity was very high, indicating that superconductivity in the pure Sr_2RuO_4 was suppressed. They make the argument that the ruthenium inclusions along the *c* axis are physically small and thus contribute very little to the measured reflectance.

Even though a significantly lower frequency was reached, no comments on ω^2 are offered within the paper. The reported optical conductivities appear roughly linear, with distinct features remaining at low temperature, in contrast to a smooth inverse parabola as would be expected for a Fermi liquid. Attempts to digitize the data presented and plot it have been inconclusive but at best do not agree with Fermi liquid theory. Due to the purity issues, the data presented within is likely of limited application to pure Sr_2RuO_4 . Furthermore, with no *ab* plane measurements, no conclusions can be made about behavior along that axis.

3.2.3 Moon *et al.*

Moon *et al.* [41] grew Sr_2RuO_4 by optical floating zone in collaboration with Dr. Maeno and others and measured the *ab* plane using reflectance spectroscopy and spectroscopic ellipsometry. X-ray absorption spectroscopy was also performed, but is not discussed here. These measurements were performed at room temperature and from $\approx 40 \text{ cm}^{-1}$ to $\approx 240000 \text{ cm}^{-1}$. This data is reproduced in figure 3.3, panel a.

First, no measurements of the purity of the sample are discussed, although based on the authors, we can assume it was measured by the Maeno group. Secondly as these measurements were only taken at room temperature, no conclusions can be drawn regarding the Fermi liquid behavior, as it only appears below ≈ 25 K. However, the general results shown in the paper can be used to corroborate any room temperature results we make in the process of our own measurements.

3.2.4 Stricker *et al.*

Stricker *et al.* [57] grew Sr_2RuO_4 by "traveling floating zone" - a separate technique from optical floating zone - and measured (by unlisted techniques) to have a superconducting transition at 1.4 K. However, the citation for the growth technique references a theory paper with no discussion of crystal growth, and so the exact technique used is unknown. They performed reflection spectroscopy from room temperature (≈ 290 K) to 9 K and from ≈ 16 cm⁻¹ to ≈ 24000 cm⁻¹ on a polished *ab* plane sample.

After measuring the reflectivity and converting to conductivity, in order to obtain the scaling relationship between ω and T in resistivity, it was assumed that $\rho = A((\hbar\omega)^2 + b(\pi k_b T)^2) = A\xi(b,\omega,T)$, with b allowed to vary. The frequency range was fixed from ≈ 16 to $\approx 290 \pm 40$ cm⁻¹. When the upper frequency limit was ≈ 290 cm⁻¹, a value of b = 4 was obtained for the minimum range of temperatures. The best value of b was determined by when the root-mean-squared deviation of b went to a minimum. b varied by as much $\approx 10\%$ as the upper frequency limit changed.

In the measurements of reflectivity, optical phonons were reported by Stricker *et al.* [57] at 323, 460 and 686 cm⁻¹. Another sharp feature appears near 363 cm⁻¹ at low temperatures, which was not reported in the main body of the paper. From inelastic neutron scattering data gathered by Braden *et al.* [7], we calculate there are optical phonons at 198.2, 366.6 and 460.3 cm⁻¹ for *c*-axis polarized measurements and 146.1, 278.8, 324.2 and 695.5 cm⁻¹ for *ab* plane measurements (as these phonons are optically active, which can be determined from the crystal structure and the rules of optical activity.

After allowing some experimental error, we conclude that Stricker *et al.* [57] are observing a mixture of both c axis and ab plane phonons. In sum, the reported phonons from Stricker *et al.* [57] suggests there are non-negligible contributions to their data from the c axis.

 Sr_2RuO_4 samples cleave easily along the *ab* plane, but can leave 'steps' of nearby layers behind, if the cleaving is done hurriedly. By polishing the sample,



Figure 3.3: The optical conductivities of the ab planes of Sr_2RuO_4 (in panel a), Sr_2RhO_4 (in panel b), and strontium iridate (214) (Sr_2IrO_4 , in panel c). Reprinted figure from Moon *et al.* [41]. Copyright 2006 by the American Physical Society.

it may be that the surface became a 'dimpled' ab plane, with many exposed areas with an ac geometry. Alternatively, the polishing may have been done at a slight angle relative to the true ab plane. If the orientation of the c axis and the wave vector of the incident light are even partially aligned, longitudinal caxis phonons can be excited and appear in reflectivity measurements [50]. In a similar anisotropic layered compound, LSCO (La_{2-x}Sr_xCuO₄), a miscut of 5° was enough to introduce c axis phonons to ab plane data [56]. In either case, this would result in a mixture of ab plane and c axis measurements.

Any scattering introduced by roughness from polishing would be negligible in the very far infrared. For example, if a one micron surface roughness was introduced, that corresponds to a photon energy of approximately 1 eV. However, in the data presented by Stricker *et al.* [57], there is a consistent increase in reflectivity when compared to data from Katsufuji *et al.* [24], and as such there is no smoking gun for poor polishing.

Another issue with the experimental conclusions presented by Stricker *et al.* [57] is that Fermi liquid-like scaling is observed up to 40 K. No papers or articles to date have ever claimed to observe Fermi liquid temperature scaling in Sr₂RuO₄ beyond, at highest, ≈ 30 K - for example as reported by Mackenzie *et al.* [32]. (Some articles claim much higher temperatures but lack appropriate references to this value, for example Kee *et al.* [25]) Thus, the purity and properties of the sample are again in doubt. 40 K is also used as the upper temperature limit in their fitting to identify the value of *b*, which may have influenced their results. In particular, we can view the insert of figure 3a in Stricker *et al.* [57] and note the downturn at the extreme left edge, corresponding to 35 K. This may indicate that as better approximations to the upper temperature limit are taken, the value of *b* actually decreases.

Finally, we take a special focus on the theoretical analysis used in Stricker et al. [57] used to determine the value of b. As mentioned above, both the temperature and frequency terms appear only appear squared in their assumed formula for the resistivity (or scattering rate), and only the scaling factor between them is allowed to change. Spectra from a range of temperatures were then used as an ensemble and compared to a linear fit to determine which scaling factor returned the most linear fit. This can be seen in figure 3b of Stricker *et al.* [57]. However, as will be described in the next section, the level of noise casts doubt on their determination of the scaling relationship of resistivity on frequency and temperature - including what powers of frequency and temperature appear in the resistivity.

On the analysis used in Stricker et al.

The data shown in the right panel of figure 2 of Stricker *et al.* [57] does not exhibit obvious ω^2 behavior in the scattering rate. However, figure 3b appears to show a scattering rate proportional to ω^2 . Both figures showed significant noise - ≈ 20 meV peak-to-peak at low frequencies - on top of a signal of ≈ 10 meV. To determine whether the data showed ω^2 scaling, we aimed to simulate the data, which also gave us better understanding of their analysis.

Using MATLAB, we wrote code that would model a scattering rate similar to that shown by Stricker *et al.* [57], depending on both photon energy and temperature, over ranges taken directly from Stricker *et al.* [57]. The function $1/\tau$ took the form:

$$1/\tau(\omega,T) = A(\hbar\omega)^B + C(\hbar\omega)^D + E(k_BT)^F + G$$
(3.2.1)

A through G were chosen manually and adjusted until a qualitative and nearlyquantitative agreement with figure 3b of Stricker *et al.* [57] was achieved. We modeled two situations - a linear frequency and temperature dependence, with B = F = 1, and a Landau-Fermi liquid-like frequency and temperature dependence, with B = F = 2. A Drude component was simulated by setting D = -4. The constants A, C, E and G were chosen to match the magnitude of $1/\tau$ from Stricker *et al.* [57]. Following this, a noise value, generated using normally distributed values combined with a frequency rolloff (for example, for pink noise, the noise max amplitude was reduced by a factor of $\sqrt{10}$ for a frequency $10 \times$ as high), is generated for each value of temperature and energy, and added to the matrix of scattering rates to simulate noise.

After generating the data, the data was plotted as a function of $\xi(b, \omega, T) = \hbar \omega^2 + b(k_b \pi T)^2$, then fit to a straight line from which the coefficient of determination R^2 (a measure of the goodness of the fit) was calculated. A variety of values of b were attempted for each simulation in order to determine which b yielded the largest R^2 value, which is displayed along with the choice of b in the x-axis label. In each of the plots, the title shows the exact equation used for $1/\tau(\omega, T)$. The simulation code is contained in appendix C.1.



Figure 3.4: A linear T and ω equation (plus a Drude-like component) which give straight looking lines when plotted as a function of $\hbar\omega^2 + 4k_b^2\pi^2T^2$ and with some pink noise. This has the highest R^2 among various other choices of b.

As we can see in figure 3.4, it is definitely possible to create a function without a quadratic dependence in either energy or temperature which approximates a straight line with b = 4 when analyzed using this method, with only 20 meV peak-to-peak of noise - which is approximately the same as that displayed in figure 3b of Stricker *et al.* [57]. In this case, a pink noise function was used.

As this is a simulation, we can remove the noise entirely and reproduce figure 3.4 without it. This is shown in figure 3.5. A distinct curvature in the data, as well as the separate temperatures not perfectly overlapping, gives away the fact that the resistivity is not a quadratic function of both energy and temperature.

In our simulation of a Landau-Fermi liquid, we used equation 2.2.2 to generate $\rho \propto 1/\tau$, again with and without noise, with the results shown respectively in figure 3.6, and figure 3.7. By comparing the figure with noise to



Figure 3.5: A linear T and ω equation (plus a Drude-like component) which give straight looking lines when plotted as a function of $\hbar\omega^2 + 4k_b^2\pi^2T^2$, but without noise. Note the subtle curvature. In the absence of the Drude-like component, the effect is most visible at low frequencies.



Figure 3.6: In this case, the scattering rate is given by a constant times $\approx ((\hbar\omega)^2 + 4(k_b\pi T)^2)$, plus some pink noise, and is plotted as a function of $((\hbar\omega)^2 + 4(k_b\pi T)^2)$. This obviously gives a linear agreement.

our earlier simulation in figure 3.4 we can see that distinguishing between the two data sets is very difficult - if not impossible - in the energy and temperature regime we use with the level of noise shown in Stricker *et al.* [57]. We argue that it is impossible to tell from the analysis performed by Stricker *et al.* [57] whether the scattering rate obeys the assumed scaling laws.

We have also obtained, via private correspondence from Stricker *et al.* [57], some low frequency data of scattering rate as a function of frequency. We have digitized this data in an attempt to confirm whether it shows quadratic behavior and fitted it to a second order polynomial. The fitting results at the two temperatures in the Landau-Fermi liquid regime - 9 and 15 K - are shown in tables 3.1 and 3.2 respectively. As is obvious from the values and uncertainties, the 15 K data is more likely to be linear than quadratic, whereas the opposite is true for the 9 K data.

We end our discussion of the work of Stricker et al. [57] by a brief summary of



Figure 3.7: In this case, the scattering rate is given by a constant times $\approx ((\hbar\omega)^2 + 4(k_b\pi T)^2)$, and is plotted as a function of $((\hbar\omega)^2 + 4(k_b\pi T)^2)$. As the dependent and independent variables are (nearly) the same, except for a scaling factor, the curves nearly overlap.

Term	Value	Uncertainty
Constant	0.0053	0.0011
Linear	0.0013	0.0012
Quadratic	1.9×10^{-5}	3×10^{-6}

Table 3.1: The results of a second order polynomial fit to 9 K data from Stricker *et al.* [57].

$15 \mathrm{K} \mathrm{Term}$	Value	Uncertainty
Constant	0.003	0.002
Linear	0.0008	0.0002
Quadratic	1×10^{-6}	4×10^{-6}

Table 3.2: The results of a second order polynomial fit to 15 K data from Stricker *et al.* [57].

the two key deficiencies of their work. First, the raw data show an unexpected contribution from c axis phonons and a larger than expected temperature range of Landau-Fermi liquid behavior. Second, the experimental data show an unexpectedly high level of noise, and the chosen analysis means that it is not possible to determine whether the scaling is linear or quadratic - in either frequency or temperature. The data also shows both linear and quadratic frequency scaling for temperatures where resistivity of the pure material is known to scale as T^2 . We conclude that the data shown by Stricker *et al.* [57] does not support their conclusion that Sr_2RuO_4 obeys Landau-Fermi liquid theory.

3.3 Overview of past Sr_2RhO_4 work

Strontium rhodate (214) (Sr₂RhO₄) was known as a 2-d conducting material as early as 1992 [54]. Simultaneously with the discovery of superconductivity in strontium ruthenate (214), strontium rhodate (214) was observed to not superconduct [35]. This has been confirmed in recent measurements as well [42]. Nonetheless a variety of similarities - and differences - between the materials have been explored. For example, Sr₂RhO₄ also shows highly anisotropic resistivity between the *ab* plane and the *c* axis, and also displays T^2 behavior below ≈ 25 K [42]. Resistivity data is shown in figure 3.8 and AC susceptibility data in figure 3.9.

Given the fact that it does not superconduct, research into Sr_2RhO_4 has not been as widespread or aggressive as Sr_2RuO_4 . Some key papers are those of Perry *et al.* [47], Baumberger *et al.* [3], Varela *et al.* [61], Itoh *et al.* [22], Hase and Nishihara [17] and Haverkort *et al.* [18]. The most detailed paper (to our knowledge) comparing the differences in electronic structure between Sr_2RhO_4 and Sr_2RuO_4 is that presented by Haverkort *et al.* [18]. One key distinction shown by Haverkort *et al.* [18] is the larger impact of spin orbit coupling on the Fermi surface for Sr_2RhO_4 . This is because of nearly degenerate bands existing near the Fermi energy for extended portions of the Fermi surface.

3.3.1 Moon *et al.*

Moon *et al.* [41] also grew Sr_2RhO_4 by the optical floating zone technique.



Figure 3.8: Figure 3a of Nagai *et al.* [42], showing the resistivity of Sr_2RhO_4 in the *ab* plane and along the *c* axis. Reproduced with permission from Nagai *et al.* [42]. Copyrighted by the Physical Society of Japan.

We can assume based on the authors it was grown and analyzed via the same technique as described either by Nagai *et al.* [42] or Perry *et al.* [47]. As with Sr_2RuO_4 , measurements were performed on the *ab* plane using reflectance spectroscopy and spectroscopic ellipsometry (along with x-ray absorption spectroscopy) at room temperature and from $\approx 40 \text{ cm}^{-1}$ to $\approx 240000 \text{ cm}^{-1}$. As in the case of Sr_2RuO_4 , the absence of characterization details (merely the statement that it was not oxygen deficient) and the lack of low temperature results means no comparisons to Fermi liquid theory can be obtained, but the data can again serve to support any room temperature measurements of our own. This data in reproduced in panel b of figure 3.3.



Figure 3.9: Figure 2a of Nagai *et al.* [42], showing the magnetic susceptibility of Sr₂RhO₄. Reproduced with permission from Nagai *et al.* [42]. Copyrighted by the Physical Society of Japan.

Chapter 4

Crystal growth

4.1 Introduction

In order to obtain accurate and reproducible results on crystalline materials, well characterized single-crystal materials should be obtained. Our setup's tolerance for small samples means a wider range of materials can be grown for experimental use. Although a variety of growth techniques exist for single crystal growth, such as solution growth or the Czochralski process, at McMaster one preferred technique is optical floating zone, supervised by Dr. Hanna Dabkowska of the McMaster Centre for Crystal Growth.

4.2 Optical floating zone crystal growth

The optical floating zone crystal growth technique was used to grow all the samples of Sr_2RuO_4 and Sr_2RhO_4 described in the remainder of this thesis. The key element of this technique is a set of high power lamps, much like a typical light bulb but many times more powerful, enclosed in large elliptical mirrors that tightly focus their power. This results in a very localized "hot spot" at their focus that can reach over 2000° C. These lamps need to be water-cooled and the mirrors themselves are also cooled, with air or water depending on the model.

This hot spot is nearly always located within a thick quartz tube - in which a ceramic feed rod and a single crystal or polycrystalline seed rod are suspended - which, at McMaster, allows controlled atmospheres up to ≈ 10 bars, and simultaneously protects crystal growers, for example from any harmful gaseous or air-suspended byproducts. The feed and seed rods are moved vertically and rotated using two motors which allows control of growth rates in increments of $\approx 0.1 \text{ mm/hr}$. In some furnaces, the lamps and elliptical mirrors are moved as well as, or instead of, the rods. An example of a typical floating zone furnace is shown in 4.1.

The rods are moved and the lamp power adjusted so that the feed rod's tip is melted, and then connected to the seed rod's tip. If the power and rate of movement are set correctly, the melted region will stabilize and become a "floating zone" - a section of molten material suspended between the two rods by surface tension. As the rods or lamps move, the zone does as well, forcing parts of the feed rod to melt into the floating zone, and parts of the zone to solidify on the seed rod. Usually this will result in the formation of several competing grains on the seed crystal, but one may eventually dominate, resulting in a single crystal growth [11].

4.3 Crystals

Two materials were grown by the author in the course of this research. The specifics of each material are discussed in their individual sections, but the general approach is the same for both and is described below.

Raw materials of high purity and known composition are obtained and set aside. Strontium carbonate (SrCO₃) is baked at 500°C to remove excess water. Then the strontium source and the other material, Rx, are mixed such that the result is a mixture with the stoichiometry $Sr_2Rx_nO_mC_2$, where *n* is controlled for the purposes of self-flux and evaporation (therefore n > 1 for these materials), and *m* is not measured or controlled.

The resulting powder is ground until well mixed, then pressed into a hard pellet or rod using a press and baked for some time at high temperature, to modify the oxidation state of Rx if necessary and induce preliminary reactions. The resulting pellet is then reground, pressed into a rod, and baked, to form a tough ceramic which is suspended in the optical furnace to serve as a feed rod. A typical feed rod might look as shown in figure 4.2 [39, 46]. The mass of the material is weighed at each step to determine the losses of material due to evaporation. This also helps indicate whether the material has absorbed water



Figure 4.1: A typical optical floating zone furnace, during the setup prior to growth. The lamp is indicated by a, the mirrors by b, the ceramic feed by c, the single crystal seed by d, and the location where the quartz tube would screw in by e.



Figure 4.2: A ceramic feed rod of Sr_2RhO_4 used for crystal growth at McMaster University. The wire is platinum, which has a sufficiently high melting point to avoid melting at the temperatures used for the growth.

or otherwise reacted. Throughout this process CO_2 should be evaporating from the strontium carbonate, reducing the mass.

The seed rod can be a crystal from a previous growth (so as to induce faster transition to single crystal growth) or a separate ceramic feed rod of the same composition as the seed if a seed crystal is not available. If neither of these options exist, ceramics with high melting points can be used as a seed rod instead. However, as these ceramics are not of the same composition as the feed, cross contamination is possible.

Following the growth, the masses of the feed and seed rod can be measured and compared to the original masses, in order to determine the amount of material lost during the growth. This can - with some assumptions - be used to determine the stoichiometry of the final material.

Since the material grown may actually be polycrystalline, or contain many competing grains, it is necessary to perform some post-growth analysis. A first step is to take a collection of optical photographs of the grown crystal, to look for cracks, defects, changes in reflectivity or color along its length, which can indicate the stoichiometry changed throughout the growth. Examples of these photographs are shown in their respective section. Following this, more advanced analysis, including x-ray diffraction, can be performed. These are shown and discussed in chapter 5.



Figure 4.3: A large sample of Sr_2RuO_4 from growth C407 grown by optical floating zone technique. The left hand tip of the lower rod segment has partially broken away, revealing shiny *ab* planes. The right hand tip of the same rod segment shows a messy polycrystalline formation from the start of the growth.

4.3.1 Sr_2RuO_4

 Sr_2RuO_4 (as shown in figure 4.3) is a member of what is called a Ruddlesden-Popper series - a crystal which obeys the chemical formula rule $(ABO_3)_x$ (AO). Specifically it is the x = 1 element of the Ruddlesden-Popper series for A= Sr and B= Ru. $x = \infty$ and x from 1 to 5 have all been grown and investigated by various groups (for example by Tian *et al.* [59]). Unfortunately these all share the common short name "strontium ruthenate" and thus the trailing 3 numbers are a necessary identifier. Example of these structures are shown in figure 4.4 [30].

Samples of Sr_2RuO_4 have the space group symmetry I4/mmm, a layered tetragonal perovskite structure with lattice parameters a = b = 3.87Å, c = 12.7Å [29], and cleave easily to reveal the ab plane. The growth direction of a single crystal is typically along an a or b axis. Due to the very different chemical bonds between the a and c axis, as well as the large lattice parameter differences, the material displays anisotropic behavior, in particular in its resistivity [35]. This is demonstrated in figure 3.1 [38]. A smooth ac plane can be obtained by cutting and polishing, based on Laue measurements.

Samples of Sr_2RuO_4 were grown using RuO_2 for Rx, cut, and characterized, under the supervision of Dr. Maeno and his group, including assistant professor



Figure 4.4: The crystal structure of some of the members of the Ruddlesden-Popper series $(ABO_3)_x$ (AO) for A = Sr and B = Ru. Reprinted from Liu [30], in accordance with the Creative Commons Attribution 3.0 Unported license.

Dr. Yonezawa and several graduate students, at the University of Kyoto, by the author, using optical floating zone techniques. Specifically, crystals were grown at high speeds (> 40 mm/hr) and in a flowing, roughly 1 atm, mixture of 50% Ar and 50% O_2 gas. Baking was done in air in all other cases. Between preparation steps, exposed raw materials, ceramics, and crystals were preserved in nitrogen gas (N₂).

Ruthenium has a very high vapor pressure at high temperatures [10]. This results in ruthenium evaporation during growth - and black powder coating the inside of the optical furnace and quartz tube. As the powder builds up, continuous power adjustments during the growth are required to maintain a consistent melt zone, and the furnace must be cleaned following the growth. The powder also damages the quartz tube irreversibly and necessitates frequent replacement, lest the required power for melting a crystal exceed that available from the lamps.

 Sr_2RuO_4 samples were also prepared to expose the *ac* plane. First, the sample was cut. The very first cuts are blind - without knowledge of the crystal's specific orientation or how it grew. The resulting sample can be measured using Laue diffraction to determine its orientation [35]. From there,



Figure 4.5: The crystals obtained from growth C405 of Sr_2RuO_4 at Kyoto University.

the sample can be repeatedly polished and remeasured using Laue to obtain the correct orientation and an appropriate surface roughness. In this case, the best-polished sample was to a one micron roughness.

During the author's time at Kyoto University, three successful floating zone runs were performed, resulting in three crystals of Sr_2RuO_4 . However, during removal from the furnace, two of these crystals broke into two pieces, resulting in five distinct samples, labeled by C405-1, C405-2, C406-1, C407-1, and C407-2. The first three numbers indicate the 'run' - that is, these were from runs 405-407 of Sr_2RuO_4 under the supervision of Dr. Maeno - and the second number indicates the 'part'. C405 is shown in figure 4.5 and C407 in figure 4.3.

4.3.2 Sr_2RhO_4

Although there was initially some confusion regarding Sr_2RhO_4 's space group, current consensus seems to be that it is $I4_1/acd$, with a = b = 5.447Å, c = 25.739Å [42] - a tetragonal perovskite with its overall structure modified and its lattice parameters elongated due to the fact that RhO₆ octahedra are rotated relative to one another, by approximately 10°. This is demonstrated in figure 4.6 [17]. Sr_2RhO_4 is also the x = 1 element of a Ruddlesden-Popper



Figure 4.6: Figure 1 from Hase and Nishihara [17]. A demonstration of the changes in the octahedral structure observed between Sr_2RhO_4 - the solid structure - and Sr_2RuO_4 - the dotted structure. The rotation of the octahedra increases the size of a unit cell, thus changing the lattice parameters and the space group symmetry. Reproduced with permission from Hase and Nishihara [17]. Copyrighted by the Physical Society of Japan.

series, with up to x = 3 having been grown by Yamaura *et al.* [63].

To the best of the author's knowledge, only three groups in the world have previously attempted growth of this material by optical floating zone techniques - Perry *et al.* [47] from the Maeno and Mackenzie groups, and Nagai *et al.* [42] from the Ikeda group - making us the 4th. There have not (to our knowledge) been prior reports of its growth direction but our results indicate that it agrees with Sr_2RuO_4 and grows along an *a* or *b* axis. Furthermore it cleaves easily along the *ab* plane. Previous research has also indicated anisotropic behavior, as predicted by the large difference in lattice parameters, particularly in resistivity. (As reported by Nagai *et al.* [42], for example, and shown in 3.8).

Samples of Sr_2RhO_4 were grown by the author under the supervision of Dr. Hanna Dabkowska and students of the McMaster Centre for Crystal Growth. The growth procedures were first adapted from those reported by Perry *et al.* [47] and Nagai *et al.* [42], modified by experience working with Sr_2RuO_4 , and then further modified through practice working on the material and discussions with members of the McMaster Centre for Crystal Growth. The final procedures were written up in step-by-step instructions for the Centre, but are also included in the appendix of this thesis, in appendix A.

Unlike Sr_2RuO_4 , which uses the raw material RuO_2 , our Sr_2RhO_4 growth

uses Rh_2O_3 . Prior to floating zone growth the 3+ rhodium must be oxidized to 4+, and all baking and growth steps were performed under flowing (in the case of baking) or 7 – 8 atm static pressure (in the case of floating zone growth) of pure, dry O₂. Crystals were grown at 10 mm/hr. Between preparation steps, raw materials, ceramics, and crystals were stored in a sealed desiccator used solely for Sr_2RhO_4 and its precursor materials, to avoid cross contamination.

Although rhodium has a lower vapor pressure than ruthenium by orders of magnitude, as can be seen in figure 4.7 [10], there was still substantial evaporation and system contamination during optical floating zone growth. This again took the form of black powder coating many of the interior surfaces of the furnace and the quartz tube, which was cleaned away following the growth. However, during growth, the system did not require power adjustments for up to 1 hour, demonstrating some longer term stability.

The resulting crystal rods were dark black in color, as shown in figure 4.8, but quickly reacted with air to form a fragile gray-white material on the outside, with the center remaining shiny and revealing facets. An example of these crystals is shown in figure 4.9, and further reacted crystals in figure 4.10. A shiny crystal was investigated with Laue diffraction to determine whether it was single crystal, and if so, what structure it had. The start of the growth was the most reacted, and it was compared to the feed material and a shiny section of crystal using powder diffraction. According to Varela *et al.* [61] as well as Nagai *et al.* [42], small changes in stoichiometry can be measured via the splitting of some x-ray diffraction peaks, due to lattice distortions. These splittings can therefore be used to measure oxygen deficiency in the crystal.

Due to evidence from powder diffraction indicating oxygen deficiency, some of the crystals were annealed in flowing O_2 at 1100° C for 50 hours. The resulting crystals appeared darker, but remained very fragile. These crystals were used in subsequent analysis as well, as discussed in chapter 5 [47, 42].



Partial vapour pressures of some of the platinum metal oxides in 1 atmosphere of oxygen

Figure 4.7: The vapor pressures of various platinum metal oxides, reprinted from Chaston [10] with permission from Johnson Matthey Plc. Note that RuO_2 is highly reactive and forms RuO_3 in these temperature regimes.



Figure 4.8: A strontium rhodate crystal resulting from single crystal growth. Some damage can be seen on the side of the rod - caused by a bubble formation during crystal growth.



Figure 4.9: Some representative crystals from the reacted rod shown in figure 4.8, taken approximately three days after the growth.



Figure 4.10: Some representative crystals from the reacted rod shown in figure 4.8 taken approximately two and a half weeks after the growth. Though some crystals appear 'white' this is merely due to the angle of the reflection of light, and all crystals were shiny black or gray.

Chapter 5

Crystal characterization

5.1 Introduction

In this chapter, all characterization work on the crystals studied within this thesis will be described and reported. Refer to chapters on theory and crystal growth (2 and 4, respectively) for information on how to interpret these results.

5.2 Sr_2RuO_4 x-ray diffraction

Powder and Laue diffraction measurements were performed on Sr_2RuO_4 samples at Kyoto University - to orient them for subsequent cutting and to make preliminary measurements of their quality. An example of a measured Laue pattern is shown in figure 5.1. By comparing to theoretical patterns, the orientation of the crystal was determined. The crystal was then transferred to a device for grinding so as to prepare a specific surface. An *ac*-plane, or the [100] plane, was prepared by imaging the sides of a crystal with a cleaved *ab*plane ([001]) and then polishing at the appropriate angle. The exact angle was measured using the Laue analysis program at Kyoto University and controlled using a goniometer which interfaced with the x-ray equipment.

Powder diffraction analysis was also performed on small fragments of the grown crystals, as shown in figures 5.2 and 5.3. This indicates the strong presence of Sr_2RuO_4 and possible weak contamination by $Sr_3Ru_2O_7$. However, the preferred purity analysis technique was AC susceptibility, and so not all crystals were examined in this way.



Figure 5.1: A Laue diffraction image of a small crystal of Sr_2RuO_4 . The 4-fold symmetry of the bright points reflects the underlying symmetry of the crystal.



Figure 5.2: A zoomed in image of the powder diffraction of two Sr_2RuO_4 samples. Note the strength of the agreement with Sr_2RuO_4 as compared to those of likely impurity phases.



Figure 5.3: A zoomed in image of the powder diffraction of two Sr_2RuO_4 samples. Note the strength of the agreement with Sr_2RuO_4 as compared to those of likely impurity phases.

5.3 Sr_2RuO_4 AC susceptibility

Due to it's well known superconducting transition and well-studied eutectic phases, Sr_2RuO_4 can have its purity investigated through AC magnetic susceptibility measurements, e.g. as shown in figure 3.2. Specifically, common impurity phases show up in the measurements as the early onset of perfect diamagnetism (suppression in the real part of the susceptibility), starting as high as 3 K, due to metallic ruthenium inclusions, known as the "3-Kelvin Phase" (or 3 K phase) [55], or as multiple superconducting transitions, with associated multiple peaks in the imaginary susceptibility and many 'steps' towards reaching diamagnetism, due to $Sr_3Ru_2O_7$ [26].

The AC susceptibility of the Sr_2RuO_4 samples grown for this study are shown in figures 5.4, 5.5, 5.6, 5.7, and 5.8, with the real part measured as V_y and the imaginary part measured as V_x , following Yaguchi *et al.* [62]. The measurements of the C405-1 sample were accidentally out of phase, and thus the data shown here has been phase corrected to generate a peak in the imaginary susceptibility. Arrows point to the beginning of diamagnetism and the cusp of the peak in the imaginary susceptibility.



Figure 5.4: The AC susceptibility of a sample from growth C405-1 as a function of temperature. The superconducting transition begins at ≈ 1.7 K and the imaginary susceptibility peak is at 1.39 K. The measurement's phase has been rotated by 0.07π to generate this more traditional looking AC susceptibility curves.

We can compare these figures to previous measured results, e.g. as presented by Maeno *et al.* [36]. For a pure crystal, we expect a sharp peak in the imaginary susceptibility, as well as a sudden sharp 'step' in the real susceptibility from a high to low value indicating the onset of diamagnetism associated with superconductivity. Assuming these sharp features exist, they tell us about the superconductivity of the Sr_2RuO_4 crystal as a whole. However, common impurities tend to smear out these features [26, 36]. In particular, the presence of $Sr_3Ru_2O_7$ will result in a small volume fraction superconducting at a different temperature than the rest of the crystal, which shows up a small dip or step in the real susceptibility [26]. The presence of the 3 K phase will tend to give a smooth decrease in the real susceptibility at some temperature above that of the remaining sharp features, and builds a 'shoulder' in the imaginary susceptibility [36]. We report in figures 5.4 through 5.8 the location of the sharp peak, as well as the first measurable temperature where diamagnetism appears, which measure, approximately, the temperature of the onset of bulk and local (impurity-driven) superconductivity, respectively.



Figure 5.5: The AC susceptibility of a sample from growth C405-2 as a function of temperature. The superconducting transition begins at ≈ 1.6 K and the imaginary susceptibility peak is at 1.37 K.



Figure 5.6: The AC susceptibility of a sample from growth C406-1 as a function of temperature. The superconducting transition begins at ≈ 1.67 K and the imaginary susceptibility peak is at 1.3 K.


Figure 5.7: The AC susceptibility of a sample from growth C407-1 as a function of temperature. The superconducting transition begins at ≈ 1.77 K and the imaginary susceptibility peak is at 1.4 K. The large dip in the real susceptibility indicates contamination by the 3 K phase.



Figure 5.8: The AC susceptibility of a sample from growth C407-2 as a function of temperature. The superconducting transition begins at ≈ 1.7 K and is strongest at 1.4 K.





5.4 Sr_2RuO_4 DC resistivity

Measurements of the DC resistance of Sr_2RuO_4 samples were performed by master's degree candidate Mahsa Rahimi of the Timusk group at McMaster University using an Oxford Cryostation physical properties measurement system. Although measurements and improvements to the system and wiring are ongoing, some preliminary measurements on a sample from C405-1 have been performed and are shown in figure 5.9. Note that the sample displays the expected quadratic behavior of resistance (and thus resistivity) on temperature, indicating it is a 'Fermi liquid' up to approximately 20 K. The fit was performed using $\rho = A + BT^2$ on data from base to 20 K.

As the data in this section was collected by Mahsa Rahimi, we have reproduced one figure containing data from the same sample from Mahsa Rahimi's thesis in figure 5.10. Note that two fits (with coefficients contained in table 5.1) are plotted here. For further details, we recommend Mahsa Rahimi's thesis.

Coefficient	Value	Uncertainty
Constant	5.1×10^{-5}	3×10^{-6}
Linear	4.4×10^{-6}	6×10^{-7}
Quadratic	8.5×10^{-7}	3×10^{-8}
Constant	$7.3 imes 10^{-5}$	1×10^{-6}
Quadratic	1.045×10^{-6}	8×10^{-9}

Table 5.1: The fitting coefficients and uncertainties from Mahsa Rahimi's fitting of data shown in figure 5.10. The first group is the linear and quadratic fitting ($\rho = A + BT + CT^2$), the second from quadratic fitting ($\rho = A + BT^2$).

What about the linear resistivity term? Berger *et al.* [5] reported linear resistivity in Sr_2RuO_4 previously, however, this has not been reproduced on crystals from floating zone furnaces. The linear coefficient can be thought of as a contaminant contribution from non-electron-electron interactions - for example, the high temperature phonon-related resistivity scales as T, as seen in section 2.2. However, this is not a high temperature regime for Sr_2RuO_4 , as confirmed from the Debye temperature reported by Paglione *et al.* [45]. Linear resistivity is also typical of heavy fermion systems near quantum critical points. Sr_2RuO_4 can in some senses be viewed as an intermediate compound between a normal metal and a heavy fermion system, as detailed by Maeno *et al.* [38] in figure 4. Further details on linear resistivity can be found in the works of Shaginyan *et al.* [51] or Bruin *et al.* [8].

All considered, we prefer the fit containing no linear terms over that containing linear terms. We know from other work to expect a quadratic term, and we note that including the linear term increases the uncertainty by approximately a factor of 3 for both the residual resistivity and the quadratic term. The linear component's largest effects occur at high temperature, where Landau-Fermi liquid behavior begins to break down anyways, and so we deem it irrelevant for the lower temperatures.

5.5 Sr_2RhO_4 powder diffraction

Following the reaction of the grown rod, as discussed near the end of section 4.3.2, the resulting small crystals were examined to determine the source of the reaction. Powder diffraction revealed that the crystals were slightly oxygen deficient Sr_2RhO_4 , from comparison to results from Varela *et*



Figure 5.10: The resistivity of a sample from C405-1 as a function of temperature. The fits were performed on data from 2 to 18 K. The coefficients with uncertainties are contained in table 5.1. Reproduced with permission from Mahsa Rahimi.

al. [61]. The gray material from the very start of the growth, and which was presumably lining the crystal based on visual comparison, was determined to contain hydrated strontium hydroxide - $Sr(OH)_2 \bullet H_2O$ - as shown in figure 5.11. Powder diffraction taken after annealing is shown in figure 5.12.

As can be seen, the annealing resulted in substantially less hydroxide appearing in the powder x-ray results - specifically, observe the absence of the peak at $\approx 40.5^{\circ}$ in figure 5.12 as compared to in figure 5.11. Although we were able to identify the main components of the crystals, the pattern was not an exact match with the ICSD data for Sr₂RhO₄ and had some very weak peaks which we were not able to identify. Several months later a repeat of the experiment was performed, with the goal of extending the data in 2θ space so as to obtain more accurate measurements of the exact crystal structure. These results are shown in figure 5.13. By comparing figures 5.12 and 5.13 in figure 5.14 we can see that the composition has not significantly changed over time, indicating that our annealed crystals are chemically inert.



Figure 5.11: Powder x-ray diffraction results of the grown Sr_2RhO_4 (in blue and red), revealing the presence of hydrated strontium hydroxide (in pink). "Varela" refers to oxygen deficient Sr_2RhO_4 data digitized from Varela *et al.* [61].



Figure 5.12: Data from the annealed Sr_2RhO_4 crystals, indicating the likely presence of Sr_4RuO_6 (In the legend as Randalt 416).



Figure 5.13: The same Sr_2RhO_4 growth, measured several months later.



Figure 5.14: A comparison of the earlier and later measurements of the same Sr_2RhO_4 growth.



Figure 5.15: Laue diffraction results from Sr_2RhO_4 .

5.6 Sr_2RhO_4 Laue diffraction

Laue diffraction was used on the reacted crystals to ensure the material was crystalline. Given the sharp peaks in the pattern, the crystalline nature was confirmed, but the diffraction pattern was insufficiently strong to make statements regarding the agreement of the grown crystal with the expected lattice. These results are shown in figure 5.15. As the reacted crystals were very fragile and broke easily to create very thin samples with large ab planes, an ac face has not yet been obtained.

5.7 Sr_2RhO_4 single crystal diffraction

Annealed samples of Sr_2RhO_4 were sent to the McMaster Analytical X-Ray Diffraction facility for measurements at ≈ 100 K and room temperature. The facility processes the data into a set of reflections in reciprocal space which were subsequently refined by the author, with assistance from Dr. Britten of the facility as well as PhD candidate Nathan Armstrong, using the Olex2 software [12]. The resulting crystal structures are shown in figures 5.16 and 5.17, along with the full reports in appendix B [34, 33, 9, 58].



Figure 5.16: The structure of Sr_2RhO_4 at room temperature as visualized by the Olex2 software and generated from single crystal diffraction data. The view is with the *ab* plane nearly into the page, tilted slightly for perspective. The light blue atoms are strontium and the red ones oxygen. The rhodium atoms are contained within the dark blue octahedra. Note that the each octahedra has a distinct orientation and is not overlapped with a second octahedra.

Of note is that the refinement did not reveal oxygen deficiencies as shown in table 5.2 - in fact, all occupancies were unity within error. Also there was no splitting of the oxygen locations, indicating that the structure is, in some sense, 'perfectly aligned', with no disorder in the layers of rotated octahedra. This is in contrast to data from the Inorganic Crystal Structure Database on Sr_2RhO_4 (for example from Itoh *et al.* [22]), which indicates that the oxygen in the *ab* plane should split, so that adjacent *ab* layers are randomly either identical in their oxygen positions or mirrored.

These results were also viewed, and a powder diffraction pattern generated,

Atom	293K	$100 \mathrm{K}$
Rh	Fixed at 1	Fixed at 1
Sr	1.008 ± 0.004	1.004 ± 0.004
O (out-of-plane)	1.03 ± 0.02	1.024 ± 0.019
O(ab plane)	1.035 ± 0.018	1.007 ± 0.018

Table 5.2: The occupancies of the various atoms in Sr_2RhO_4 as measured by single crystal diffraction.



Figure 5.17: The structure of Sr_2RhO_4 at ≈ 100 K as visualized by the Olex2 software and generated from single crystal diffraction data. The view is with the *ab* plane nearly into the page, tilted slightly for perspective. The light blue atoms are strontium and the red ones oxygen. The rhodium atoms are contained within the dark blue octahedra. Note that the each octahedra has a distinct orientation and is not overlapped with a second octahedra.

using the Mercury visualization program and compared to our existing powder diffraction data, shown in 5.18 [34, 33, 9, 58].

5.8 Sr_2RhO_4 magnetization

SQUID measurements were performed at McMaster University on Quantum Design Magnetic Property Measurement Systems (MPMS). The Luke group first measured the magnetic susceptibility of Sr_2RhO_4 as a function of temperature. The measurements were also repeated by technician Paul Dube on a separate SQUID and revealed different results, as shown in figure 5.19. The first difference between the two measurements is the orientation of the crystal - in the Luke SQUID, the crystal was oriented so that the magnetic field was applied along the *a* direction. In the Dube SQUID, the crystal was oriented along the *b* direction. As *a* and *b* are supposed to be equivalent in Sr_2RhO_4 , this implies the impurity phase is not of the same crystal structure as Sr_2RhO_4 .

A second difference was in the way cooling was performed. In the mea-



Figure 5.18: A zoomed in powder diffraction result from Sr_2RhO_4 as compared to simulated powder diffraction data generated by Mercury.

surements performed on the Luke SQUID, the sample was rapidly cooled to the base temperature, and then warmed up to room temperature as data was collected, for both sets of measurements. On the Dube SQUID, the sample was rapidly cooled to the base temperature prior to the zero field cooled experiment. As data was collected, the sample was warmed up slowly. Upon reaching the maximum temperature of data collection (≈ 100 K), it was then cooled down during data collection in the zero field cooled experiment. The effectively longer cooling time smoothed out the sharp feature near 45 K. Cooling to the base temperature more slowly prior to the zero field cooled experiment smoothed the feature out even more. However this had very little effect on results in the field cooling experiment. This is shown in figure 5.20.

All measurements were quite different from previous measurements such as those by Nagai *et al.* [42], reproduced in figure 3.9. The key difference is the feature at ≈ 45 K. This is a temperature regime associated with a magnetic transition in solid oxygen. Although the reproducibility of the results does not lend credence to the argument of oxygen contamination, the fact that the transition is smoothed out as the rate of cooling changes does. It remains inconclusive whether the results are real, or merely the result of some sort of contaminant [48].



Figure 5.19: The magnetic susceptibility of Sr_2RhO_4 as compared between two different SQUIDs. The two measurements were made at different rates of cooling and with different orientations.



Figure 5.20: A comparison of the AC magnetic susceptibility of Sr_2RhO_4 as the rate of cooling is changed. Zero field cooled data is obtained by cooling to 2 K then warming. The difference between 'rapid' and 'slow' is that 'rapid' cooling occurred at 1 K per minute, but 'slow' cooling occurred at 0.1 K per minute. Field cooled data is obtained by cooling from 100 K - the end of the zero field cooling data - to 2 K while collecting data, so the effective cooling rate is always very slow.

Chapter 6

Optical measurements

6.1 Introduction

Two separate techniques were used to obtain optical measurements on Sr_2RuO_4 and Sr_2RhO_4 - spectroscopic ellipsometry and reflection spectroscopy. Each is located within a separate section. Spectroscopic ellipsometry measurements were heavily assisted by PhD candidate Nathan Armstrong.

6.2 Spectroscopic ellipsometry

Spectroscopic ellipsometry measurements were performed on the *ab* face of a crystal from growth C407-1 and on the polished *ac* face of a crystal from C405-2 at room temperature with frequencies from ≈ 6000 to ≈ 40000 cm⁻¹ using a J. A. Woollam M2000UI variable angle spectroscopic ellipsometer owned by the Centre for Emerging Device Technology at McMaster University. Sizes of the samples were measured using a ruler in order to provide the analysis software with a 'first-guess' for analysis. Some typical ψ and Δ are shown in figures 6.1 and 6.2, respectively.

Following data collection, data was fit a to a series of oscillators by Nathan Armstrong - typically Lorentzian oscillators, though other oscillators, such as Gaussian oscillators, were occasionally used. The results of the fit are compared with Δ , ψ , and material parameters such as ϵ . Following an adequate fit, surface roughness could be included in the model. The resulting model of optical properties was used to generate ϵ , which was subsequently used to



Figure 6.1: ψ for Sr₂RuO₄ ab plane as measured by variable angle spectroscopic ellipsometry.



Figure 6.2: Δ for Sr₂RuO₄ ab plane as measured by variable angle spectroscopic ellipsometry.



Variable Angle Spectroscopic Ellipsometric (VASE) Data

Figure 6.3: $< \epsilon_2 > \text{of } \text{Sr}_2 \text{RhO}_4$ as calculated directly from ψ and Δ using equation 2.5.1 for each angle of the variable angle ellipsometer.

generate the conductivity.

As a check, equation 2.5.1 was used to visualize the spread of the calculated ϵ values with angle. If we were probing something that depended on the angle of incident light - for example, surface roughness, an extra surface layer, or in our case the *c*-axis - there would be a spread or divergence of the data with a change in probe angle. Usually the contribution of the *c* axis was small and so was ignored. An example of this spread is shown for Sr₂RhO₄ in the pseudodielectric function $\langle \epsilon_2 \rangle$ in figures 6.3 and 6.4. The fact that the spread is small indicates that the contribution from the *c*-axis can be ignored.

The conductivities (as a function of frequency) for the ab-plane of Sr_2RuO_4 and the ab-plane of Sr_2RhO_4 are shown in figures 6.5 and 6.6 respectively. The Sr_2RuO_4 ac plane sample has been measured as well, however, analysis has proven more challenging and is ongoing. A preliminary result is shown in figure 6.7.

By comparing the (reliable) data to that presented in, for example, Moon $et \ al. \ [41]$ - discussed and shown in section 3.2.3 - we see good agreement, including reproduction of the key features such as the locations of bumps and valleys in the real part of the conductivity. The absolute magnitude of the conductivity does not precisely agree, however, this may simply be a side effect



Variable Angle Spectroscopic Ellipsometric (VASE) Data

Figure 6.4: $< \epsilon_2 >$ of Sr₂RhO₄ as calculated directly from ψ and Δ using equation 2.5.1 for each angle of the variable angle ellipsometer. Note the zoomed x scale as compared to figure 6.3.

of the modeling or the difference in samples.

6.3 Reflection spectroscopy

Some optical measurements were performed with the Bruker, described in section 2.4, on ab and ac plane samples from growth C407-2, as well as an ab plane of Sr_2RhO_4 . The first measurements were performed using the 4 K bolometer and the globar. The polarization of the light was controlled to only probe the c axis of the ac face sample. Unfortunately the measured reflectivity for the metallic samples - the ab planes of Sr_2RuO_4 and Sr_2RhO_4 displayed reflectivity above 100%, and noise higher than 1%, neither of which are acceptable. The reflectivity data is shown in figures 6.8 through 6.10, and has been adjusted in magnitude to both lower it below the 100% level and to bring the magnitude of the ab plane data in line with that reported by Stricker et al. [57].

The issue with the noise could be resolved by scanning longer. However, the issue with the reflectivity being higher than 100% implies either problems with the gold evaporation (e.g. the sample only being partially coated with



Figure 6.5: Optical conductivity of the ab plane of a Sr_2RuO_4 sample from C407-2, measured via ellipsometry.



Figure 6.6: Optical conductivity of the ab plane of a Sr_2RhO_4 sample from the first growth at McMaster. Note that there was no surface roughness assumed in this analysis. Fitting for surface roughness resulted in behavior which was deemed unrealistic - for example, conductivities approximately $3 \times$ higher than previously reported.



Figure 6.7: Optical conductivity of the c axis of a polished ac plane Sr_2RuO_4 sample from C407-2, measured via ellipsometry. The a axis contribution has been removed by using data from previous measurements, for example that shown in figure 6.5. The data was analyzed wavelength-by-wavelength and thus is not reliable quantitatively, however, qualitatively the data is in agreement with that shown in Katsufuji *et al.* [24]. The surface was polished to 1 µm roughness.



Figure 6.8: 4 K bolometer data from September 18th 2013 showing Sr_2RuO_4 ab data. Data has been adjusted 2% downwards to agree in magnitude with data presented by Stricker *et al.* [57].



Figure 6.9: 4 K bolometer data from September 18th 2013 showing $Sr_2RuO_4 c$ axis data. The large features in the *ac* data occur at 198, 373, and $\approx 500 \text{ cm}^{-1}$ and are optical phonons - in agreement with results reported by Katsufuji *et al.* [24]. Data has been adjusted 2% downwards to agree in magnitude with *ab* plane Sr_2RuO_4 data presented by Stricker *et al.* [57].



Figure 6.10: 4 K bolometer data from September 18th 2013 showing Sr_2RhO_4 *ab* data. Data has been adjusted 2% downwards to agree in magnitude *ab* plane Sr_2RuO_4 data presented by Stricker *et al.* [57].

gold) or alternatively instability in the detector. The detector naturally drifts as its temperature changes, however, measurements which appear as ratios are usually taken close together in time, so that drift is minimized. Although this technique was adopted in these measurements, it obviously did not work.

Measurements were then attempted in the very far infrared - using the 1K bolometer and the mercury arc lamp. Unfortunately the detector ran out of helium partway through the run, and so the measurements were not complete. Of the data that exists, it was extremely noisy - displaying square features, inconsistent behavior with temperature, and large features which did not exist in previous data. A subsequent run attempted to fill in the missing data, but ultimately encountered similar problems. Measurements on the 1K bolometer were fraught with noise issues, related to temperature control issues and wiring problems, which remain under investigation, and so the measurements are not necessarily trustworthy. During the writing of this thesis, a possible cause of these problems was located and the detector may be fully operation soon.

Measurements were also performed in the mid-infrared using the MCT detector, however, the evaporation of gold was unsuccessful for the ab plane of Sr₂RuO₄ and Sr₂RhO₄, so the data was not usable. Data from the c axis is shown in figure 6.11. A subsequent run on the MCT collected ab plane data on both Sr₂RuO₄ and Sr₂RhO₄, but only at room temperature, shown in figure 6.12.

All in all, the available data on Sr_2RuO_4 and Sr_2RhO_4 are isolated frequency regimes - there is not enough data to make use of the Kramers-Kronig relation in a reasonable way. Measurements of the optical conductivity from reflection spectroscopy are not available at the time of submission.



Figure 6.11: MCT data from January 27th 2014. $\rm Sr_2RuO_4\ c$ axis data is shown.



Figure 6.12: MCT data from February 20th 2014. Sr_2RuO_4 and Sr_2RhO_4 *ab* plane data is shown, in red and blue respectively. Data collected by Jesse Hall.

Chapter 7

Discussion and conclusions

Let us begin by reviewing what we set out to do. Our goal was to make measurements of the Landau-Fermi liquid behavior in $\rho(\omega)$ for both strontium ruthenate (214) (Sr₂RuO₄) and strontium rhodate (214) (Sr₂RhO₄), which are widely believed to be Landau-Fermi liquids but there is a lack of evidence for the appropriate $\rho(\omega)$ behavior. We also needed to understand our samples and their purity, so that we could make these arguments on materials that fit into the existing research.

We have succeeded in growing samples of both Sr_2RuO_4 and Sr_2RhO_4 and have characterized them in detail. Our Sr_2RuO_4 samples still have some 3 K phase, but all measurements of superconductivity show a significant volume fraction begins superconducting only extremely near to 1.5 K, the accepted superconducting transition temperature for Sr_2RuO_4 . Our Sr_2RhO_4 samples show a novel magnetic impurity which has both a very long relaxation time and a structure which does not follow that of the underlying crystals. It is likely an extremely small fraction, due to the completeness of the x-ray data in demonstrating the absence of magnetic impurities - though some impurities remain.

We have argued that existing optical data on both of these materials is insufficient, but failed to substantially improve on the situation. Although reflection spectroscopy measurements will continue past this thesis, they are not yet at a complete enough state to make any statements regarding $\rho(\omega)$, except in the most tenuous (and fallible) way. Therefore we have failed in our primary goal. However, we have laid the groundwork for future work on these materials in the Timusk lab, in which measurements will continue. The primary problems in sample purity cannot merely be resolved by better growth. The existence of the 3 K phase is an unfortunate side effect of the ruthenium over-doping and the difficulty in perfect reproducibility of furnace heating profiles. The magnetic impurity in Sr_2RhO_4 is not yet detectable by any means beyond magnetic susceptibility, which does not tell us anything about its composition. At the present time it is a mystery which might only be resolved by techniques such as transmission electron microscopy (TEM). However, even TEM may be of limited applicability, as an extremely small sample is required for the technique. If the impurity phase is highly localized - for example, a bubble of unreacted material from the floating zone growth contained within our bulk crystal - it is possible that TEM will reveal nothing unless the impurity is also present within the very small subsection of the crystal measured.

In conclusion, although we have not successfully validated - or invalidated - the applicability of Landau-Fermi liquid theory to Sr_2RuO_4 or Sr_2RhO_4 , we have been able to characterize the materials to a high standard. Thus, we have successfully laid the groundwork for future work in the Timusk lab on these materials. The immediately obvious next steps are to continue low temperature reflection spectroscopy measurements of the samples in order to satisfy this goal.

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Appendices

Appendix A

Crystal growth guides

Note that the template for Sr_2RuO_4 is partially in Japanese. Translations for individual sections are provided.

A.1 Sr_2RuO_4

This rough translation starts from page one, shown in figure A.1. The first block after the header describes the pre-heating of strontium carbonate to remove water. The Japanese text above the chemical formula is 'prebake'. Inside the box, the Japanese text is 'manufacturer data'. The second block describes the pre-reaction. The box with weight in brackets below the manufacturer data is to be used for the calculated amount of strontium carbonate necessary, followed by the actual amount used. The last block on page one is about ceramic formation. Page two (in figure A.2) is dedicated to the actual floating zone crystal growth, including sections for notes and observations about the growth process.



Figure A.1: Page one of the Sr_2RuO_4 growth template.



Figure A.2: Page two of the Sr_2RuO_4 growth template.

A.2 Sr_2RhO_4

As I prepared this growth template myself, I have written additional stepby-step instructions on the growth of Sr_2RhO_4 , which are compiled below.

A.2.1 Step-by-step instructions

- 1. Always remember to wear gloves and clean them with ethanol.
- 2. Clean all equipment. Label anything you think you will need to use multiple times if you're going to make an irreversible change to it. Label with CHEMICAL FORMULA. Before using a new object, check whether there is an appropriate old object that you can use. Mortar and pestle will require acid cleaning if it's not specifically for this material.
- 3. Estimate required material. 15 grams will make about 8 inches of rod material, for example. For the second bake you will probably require less.
- 4. Take $SrCO_3$ crucible, weigh it, figure out if you have enough material, and if not contact Hanna.
- 5. Mark your $SrCO_3$ source in your notes!
- 6. Bake to remove H_2O .
- 7. Weigh resulting $SrCO_3$.
- 8. Mark your rhodate source bottle. Specifically, mark with your name and the date you opened it. Your notes will have information on how much remains in the bottle. If they're supposed to be empty, put a new label on it.
- 9. Weigh desired Rh₂O₃ and add to mortar. Current best approach: Weigh a bottle, and then transfer directly from bottle to mortar using a clean scoopula. Be careful, don't waste material! Remember to reseal your Rh₂O₃ with electrical tape once you're done.
- 10. Add $SrCO_3$ in the desired concentration to the rhodate. Remember that you probably lost some rhodate in the transfer too, so don't be too afraid of being a little under. Current best approach: Take a piece of clean



Figure A.3: Page one of the Sr_2RhO_4 growth template.



Figure A.4: Page two of the Sr_2RhO_4 growth template.

paper, put on the balance, tare, and put SrCO3 from crucible onto paper, then pour paper in mortar. Do this with the $SrCO_3$ as hot as possible, so there is less time for it to reabsorb water.

- 11. If possible, seal the mixture in a plastic bag that has been evacuated with N_2 . This is to reduce the effect of atmospheric moisture on the mixture.
- 12. Mix for at least one hour in the mortar and the sealed bag. Remember to mix gently at the start so you don't affect stoichiometry. Your goal at this point is to remove any inconsistent components. For the first growth this will be white powder from SrCO3 among black powder, and for the second this will be hard lumps or shiny bits. (I'm still not sure what they are. Early ceramic formation, maybe?)
- 13. Take a 5 mm diameter balloon and a glass rod. These will serve to form your rod. Clean the rod, the inside and outside of the balloon with ethanol. (Use the rod to support the balloon's shape and turn it inside out.)
- 14. Fill balloon with mixture, keeping the material tightly packed at all stages and uniformly distributed. For packing, you can use the rod to assist you, but the approach I find works best is moving the material to the bottom of the rod, then rolling the tip between two fingers as you move them downwards, pressing the material together - possibly expanding the balloon as you do so. In Japan we used a dedicated plastic funnel to pour the material into the balloon. Here we have a glass funnel, so make sure it's well cleaned before and after you use it!
- 15. Place a loose knot in the balloon just above the end of the mixture.
- 16. Vacuum pump on the mixture using the appropriate tubing to prevent cross contamination. Roll the rod as you do this you want it to be straight and uniform still!
- 17. Tie the knot, and then tie a second knot above it while still under vacuum to prevent air from entering.
- 18. Place the tube inside a suitably sized plastic container, and tape one knot to the outside of it.

- 19. Press balloon in hydrostatic press. Current procedure is 60 MPa for 10 minutes. Be careful in ramping up and down the pressure no sudden changes!
- 20. Remove balloon from press, dry, and gently remove balloon with scissors to expose rod. Be very gentle when removing the balloon and moving the rod!
- 21. Place rod(s) on bedded crucible and perform first bake. This is currently Program 3 on the relevant McMaster furnace. Make sure to purge first and that the elements turn on as expected. Weigh your rod in the crucible before and after your bake!
- 22. Clean up your work area.
- 23. Remove rod(s) and place in mortar.
- 24. Repeat steps 11 through 22.
- 25. Place rod(s) on bedded crucible and perform 2nd bake. Again make sure to weigh and clean!
- 26. Remove rod(s)
- 27. Prepare floating zone furnace mounting equipment. (e.g. cromel holding wires)
- 28. Seal rods in nitrogen environment until floating zone furnace is ready.
- 29. Clean up your work area.
- 30. Clean floating zone furnace.
- 31. Remove rods from nitrogen and weigh them once fully mounted.
- 32. Load rods in the furnace.
- 33. Prepare atmosphere + any static variables (e.g. rotation speed).
- 34. Begin floating zone growth.
- 35. Remove rods and weigh them again.

- 36. Clean floating zone furnace rhodium evaporates, so make sure to clean all inlets and outlets.
- 37. Clean your equipment.
- 38. Anneal if necessary.

Appendix B

Structural refinement reports

This section contains the refinement reports from Olex2 [12, 52]. Due to the size of the various tables and formatting issues, these have been inserted as direct print outs.

B.1 Room temperature measurements

Sr2RhO4

Table 1 Crystal data and structure	refinement for Sr2RhO4					
Identification code	Identification code Sr2RhO4					
Empirical formula	O ₄ RhSr ₂					
Formula weight	342.15					
Temperature/K	296.15					
Crystal system	tetragonal					
Space group	I4 ₁ /acd					
a/Å	5.4417(5)					
b/Å	5.442					
c/Å	25.752(2)					
$\alpha/^{\circ}$	90					
β/°	90					
$\gamma/^{\circ}$	90					
Volume/Å ³	762.58(16)					
Z	1					
$\rho_{calc} mg/mm^3$	0.745					
m/mm ⁻¹	4.002					
F(000)	153.0					
Crystal size/mm ³	$0.481\times0.364\times0.096$					
Radiation	MoK α ($\lambda = 0.71073$)					
2Θ range for data collection	6.328 to 90.598°					
Index ranges	-10 \leq h \leq 10, -10 \leq k \leq 10, -51 \leq l \leq 51					
Reflections collected	11354					
Independent reflections	807 [$R_{int} = 0.0589, R_{sigma}$	= 0.0265]				
Data/restraints/parameters	807/0/22					
Goodness-of-fit on F^2	1.230					
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0416, WR_2 = 0.066$	2				
Final R indexes [all data]	$R_1 = 0.0724, wR_2 = 0.076$	9				
Largest diff. peak/hole / e Å-	³ 2.07/-2.50					



Table 2 Fractional Atomic Coordinates (×10 ⁴) and Equivalent Isotropic Displacement Parameters (Å ² ×10 ³) for Sr2RhO4. U	Jeq
is defined as 1/3 of of the trace of the orthogonalised U_{II} tensor.	

Atom	x	У	z	U(eq)
Rh1	5000	2500	6250	3.51(11)
Sr2	5000	7500	5509.5(2)	7.63(12)
01	5000	2500	5451.3(12)	9.2(8)
03	2952(5)	-452(5)	6250	10.4(7)

Table 3 Anisotropic Displacement Parameters (Å²×10³) for Sr2RhO4. The Anisotropic displacement factor exponent takes the form: $-2\pi^{2}[h^{2}a^{*2}U_{11}+2hka^{*}b^{*}U_{12}+...]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Rh1	3.40(13)	3.40(13)	3.71(14)	0	0	0
Sr2	8.6(4)	8.9(4)	5.39(16)	0	0	1.9(2)
01	1.6(19)	22(3)	4.3(9)	0	0	0.0(17)
03	7.6(9)	7.6(9)	15.8(15)	-0.1(15)	-0.1(15)	-2.4(10)

Table 4 Bond Lengths for Sr2RhO4.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Rh1	Sr2	3.3226(2)		Sr2	O1 ¹⁰	2.7250(3)
Rh1	Sr2 ¹	3.3226(3)		Sr2	O1 ¹¹	2.474(3)
Rh1	Sr2 ²	3.3226(2)		Sr2	01	2.72498(18)
Rh1	Sr2 ³	3.3226(3)		Sr2	O3 ¹²	2.966(3)
Rh1	$\mathrm{Sr2}^4$	3.3226(3)	1	Sr2	O3 ⁶	2.474(3)
Rh1	Sr2 ⁵	3.3226(2)	;	Sr2	O3 ⁴	2.966(3)
Rh1	01	2.057(3)		Sr2	O3 ⁹	2.474(3)
Rh1	01 ⁴	2.057(3)		01	Sr2 ¹³	2.7250(3)
Rh1	O3 ⁶	1.9551(7)		01	Sr2 ¹¹	2.474(3)
Rh1	O3 ⁷	1.9551(8)		01	Sr2 ⁵	2.72498(18)
Rh1	O3 ⁴	1.9551(8)		01	Sr2 ³	2.7250(3)
Rh1	03	1.9551(7)		03	Rh1 ³	1.9551(8)
Sr2	Rh1 ⁸	3.3226(3)		03	Sr2 ³	2.966(3)
Sr2	Rh1 ⁹	3.3226(2)		03	Sr2 ¹	2.966(3)
Sr2	O1 ⁸	2.7250(3)		03	Sr2 ¹⁴	2.474(3)
Sr2	01 ⁹	2.72498(19)		03	Sr2 ⁵	2.474(3)

 $^{1} \cdot 3/4 + Y, 3/4 - X, 5/4 - Z; \ ^{2} \cdot 1/4 + Y, 1/4 + X, 5/4 - Z; \ ^{3} 1/2 - X, -1/2 + Y, + Z; \ ^{4} 1/4 + Y, 3/4 - X, 5/4 - Z; \ ^{5} + X, -1 + Y, + Z; \ ^{6} 1 - X, 1/2 - Y, + Z; \ ^{7} 3/4 - Y, -1/4 + X, 5/4 - Z; \ ^{8} 3/2 - X, 1/2 + Y, + Z; \ ^{9} + X, 1 + Y, + Z; \ ^{10} 1/2 - X, 1/2 + Y, + Z; \ ^{11} 1 - X, 1 - Y, 1 - Z; \ ^{12} 3/4 - Y, 3/4 + X, 5/4 - Z; \ ^{13} 3/2 - X, -1/2 + Y, + Z; \ ^{10} 1/2 - X, 1/2 + Y, + Z; \ ^{11} 1 - X, 1 - Y, 1 - Z; \ ^{12} 3/4 - Y, 3/4 + X, 5/4 - Z; \ ^{13} 3/2 - X, -1/2 + Y, + Z; \ ^{10} 1/2 - X, 1/2 + Y, + Z; \ ^{11} 1 - X, 1 - Y, 1 - Z; \ ^{12} 3/4 - Y, 3/4 + X, 5/4 - Z; \ ^{13} 3/2 - X, -1/2 + Y, + Z; \ ^{14} - 1/4 + Y, -3/4 + X, 5/4 - Z; \ ^{12} - X, 1/2 + Y, + Z; \ ^{12} - X, 1/2 + Y, 1/2$

Table 5 Bond Angles for Sr2RhO4.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Sr2	Rh1	Sr2 ¹	70.766(6)	01	Sr2	Rh1 ⁸	148.13(7)
Sr2	Rh1	Sr2 ²	70.053(11)	O1 ¹¹	Sr2	Rh1 ⁹	148.13(7)
Sr2	Rh1	Sr2 ³	109.234(6)	01 ¹¹	Sr2	Rh1 ⁸	91.81(4)
$\mathrm{Sr2}^4$	Rh1	Sr2 ³	109.234(6)	O1 ¹⁰	Sr2	O1 ¹¹	86.85(7)
Sr2	Rh1	Sr2 ⁴	109.947(11)	O1 ¹⁰	Sr2	01	86.85(7)
Sr2 ¹	Rh1	Sr2 ⁵	180.0	01	Sr2	O1 ⁸	173.69(14)
Sr2 ²	Rh1	Sr2 ³	70.766(6)	01	Sr2	O1 ¹¹	89.826(8)
$\mathrm{Sr2}^{1}$	Rh1	Sr2 ⁴	70.766(6)	O1 ¹⁰	Sr2	O1 ⁸	86.85(7)
Sr2 ¹	Rh1	Sr2 ²	109.234(6)	O1 ¹⁰	Sr2	O1 ⁹	86.85(7)
Sr2	Rh1	Sr2 ⁵	109.234(6)	O1 ⁹	Sr2	O1 ⁸	89.826(8)
$\mathrm{Sr2}^4$	Rh1	Sr2 ²	180.0	01	Sr2	O1 ⁹	89.827(8)
Sr2 ⁵	Rh1	Sr2 ²	70.766(6)	0111	Sr2	01 ⁹	173.69(14)

$\mathrm{Sr2}^5$	Rh1	$Sr2^3$	109.947(12)	01^{11}	Sr2	018	89.826(8)
$Sr2^1$	Rh1	$Sr2^3$	70.053(12)	01^{10}	Sr2	03^{12}	130.02(6)
$Sr2^4$	Rh1	$Sr2^5$	109.234(6)	01 ¹¹	Sr2	03^{12}	125.18(6)
01^{5}	Rh1	$Sr2^4$	125.026(6)	01 ⁹	Sr2	03^{5}	125.18(6)
01	Rh1	Sr2	54.974(6)	018	Sr2	03^{12}	59.65(6)
01	Rh1	Sr2 ⁵	125.026(6)	01	Sr2	03^{12}	125.18(6)
015	Rh1	$Sr2^1$	125.027(6)	019	Sr2	03^{12}	59.65(6)
01	Rh1	$Sr2^4$	54.974(6)	01	Sr2	03 ⁵	59.65(6)
015	Rh1	$Sr2^2$	54.974(6)	01 ¹⁰	Sr2	03 ⁵	130.02(6)
01^5	Rh1	$Sr2^3$	54.974(6)	018	Sr2	03^{5}	125.18(6)
01	Rh1	$Sr2^1$	54.974(6)	01 ¹¹	Sr2	03^{5}	59.65(6)
01 ⁵	Rh1	$Sr2^5$	54.974(6)	03^{5}	Sr2	Rh1 ⁸	94.27(4)
01^5	Rh1	Sr2	125.026(6)	03^{12}	Sr2	Rh1 ⁹	35.657(7)
01	Rh1	$Sr2^3$	125.026(6)	03^{5}	Sr2	Rh1 ⁹	94.27(4)
01	Rh1	$Sr2^2$	125.026(6)	03^{6}	Sr2	Rh1 ⁸	85.79(6)
01	Rh1	01 ⁵	180.0	03 ⁸	Sr2	Rh1 ⁸	35.777(11)
03	Rh1	$Sr2^2$	132.28(8)	03^{12}	Sr2	Rh1 ⁸	35.657(7)
03 ⁶	Rh1	$Sr2^2$	47.72(8)	03 ⁸	Sr2	Rh1 ⁹	85.79(6)
03 ⁵	Rh1	$Sr2^1$	47.72(8)	03^{6}	Sr2	Rh1	35.777(11)
03 ⁵	Rh1	$Sr2^5$	132.28(8)	03 ⁸	Sr2	Rh1	85.79(6)
03	Rh1	Sr2	132.28(8)	03^{12}	Sr2	Rh1	94.27(4)
03 ⁶	Rh1	Sr2 ⁵	62.17(9)	03^{5}	Sr2	Rh1	35.657(7)
03 ⁵	Rh1	$Sr2^2$	62.17(9)	03^{6}	Sr2	Ph1 ⁹	35.777(11)
03 ⁵	Rh1	$Sr2^4$	117.83(9)	03^{6}	Sr2	01 ⁹	65.96(8)
03^{6}	Rh1	Sr2	47.72(8)	03^{6}	Sr2	01^{10}	140.42(8)
03	Rh1	Sr2 ⁵	117.83(9)	03 ⁸	Sr2	01^{10}	140.42(8)
03 ⁷	Rh1	$Sr2^4$	62.17(9)	03^{6}	Sr2	018	119.49(7)
03^{7}	Rh1	$Sr2^3$	132.28(8)	03 ⁸	Sr2	01	119.49(7)
03^{7}	Rh1	$Sr2^2$	117.83(9)	03^{6}	Sr2	01 ¹¹	119.49(7)
03^{5}	Rh1	$Sr2^3$	47.72(8)	03 ⁸	Sr2	018	65.96(8)
03	Rh1	$Sr2^3$	62.17(9)	03 ⁸	Sr2	01 ¹¹	65.96(8)
03 ⁷	Rh1	$Sr2^1$	132.28(8)	03 ⁸	Sr2	01 ⁹	119.49(7)
03^{7}	Rh1	$Sr2^5$	47.72(8)	03^{6}	Sr2	01	65.96(7)
03	Rh1	$Sr2^1$	62.17(9)	03^{6}	Sr2	03^{12}	60.291(7)
03^{6}	Rh1	$Sr2^4$	132.28(8)	03 ⁸	Sr2	03^{5}	60.291(7)
03^{6}	Rh1	$Sr2^1$	117.83(9)	03^{12}	Sr2	03 ⁵	99.97(11)
03^{7}	Rh1	Sr2	117.83(9)	03^{6}	Sr2	03 ⁸	79.16(15)
03^{5}	Rh1	Sr2	62.17(9)	03^{6}	Sr2	03^{5}	60.291(8)
03	Rh1	$Sr2^4$	47.72(8)	03 ⁸	Sr2	03^{12}	60.291(8)
03^{6}	Rh1	$Sr2^3$	117.83(9)	Rh1	01	Sr2 ¹⁰	180.0
03	Rh1	01	90.0	Rh1	01	$Sr2^1$	86.85(7)
03^{7}	Rh1	01 ⁵	90.0	Rh1	01	Sr2	86.85(7)
03^{6}	Rh1	01^5	90.0	Rh1	01	Sr2 ⁴	86.85(7)
03^{6}	Rh1	01	90.0	Rh1	01	Sr2 ¹³	86.85(7)
03	Rh1	01 ⁵	90.0	Sr2 ¹³	01	$Sr2^4$	89.827(8)
03 ⁵	Rh1	01^5	90.0	Sr2 ¹⁰	01	$Sr2^{13}$	93.15(7)
03 ⁵	Rh1	01	90.0	Sr2 ¹⁰	01	Sr2 ¹	93.15(7)
05	1	<i>.</i>		512		512	/ - /

O3 ⁷	Rh1	01	90.0	Sr2 ¹³	01	Sr2 ¹	173.69(14)
O3 ⁶	Rh1	O3 ⁵	90.000(5)	Sr2 ⁴	01	Sr2 ¹	89.827(8)
O3 ⁶	Rh1	03	180.0	Sr2 ¹⁰	01	Sr2	93.15(7)
O3 ⁵	Rh1	03	90.000(5)	Sr2 ¹	01	Sr2	89.827(8)
O3 ⁶	Rh1	O3 ⁷	90.000(6)	Sr2 ¹³	01	Sr2	89.827(8)
O3 ⁷	Rh1	03	90.000(5)	Sr2 ⁴	01	Sr2	173.69(14)
O3 ⁷	Rh1	O3 ⁵	180.0	Sr2 ¹⁰	01	$Sr2^4$	93.15(7)
Rh1 ⁸	Sr2	Rh1	109.948(12)	Rh1 ¹	03	Rh1	159.5(2)
Rh1 ⁹	Sr2	Rh1 ⁸	70.766(6)	Rh1 ¹	03	Sr2 ³	82.18(10)
Rh1 ⁹	Sr2	Rh1	70.766(6)	Rh1 ¹	03	Sr2 ¹⁴	96.50(7)
O1 ¹⁰	Sr2	Rh1 ⁹	125.026(7)	Rh1	03	Sr2 ¹	82.18(10)
01 ⁹	Sr2	Rh1 ⁸	91.81(4)	Rh1	03	Sr2 ³	82.18(10)
O1 ⁸	Sr2	Rh1 ⁸	38.18(7)	Rh1 ¹	03	Sr2 ¹	82.18(10)
01 ⁹	Sr2	Rh1	91.81(4)	Rh1 ¹	03	$Sr2^4$	96.50(7)
01 ¹¹	Sr2	Rh1	91.81(4)	Rh1	03	$\mathrm{Sr2}^4$	96.50(7)
01	Sr2	Rh1	38.18(7)	Rh1	03	$Sr2^{14}$	96.50(7)
01 ⁹	Sr2	Rh1 ⁹	38.18(7)	Sr2 ⁴	03	Sr2 ³	169.59(13)
01 ¹⁰	Sr2	Rh1 ⁸	125.026(6)	Sr2 ¹⁴	03	Sr2 ¹	169.59(13)
01	Sr2	Rh1 ⁹	91.81(4)	Sr2 ¹⁴	03	Sr2 ³	89.56(3)
O1 ⁸	Sr2	Rh1 ⁹	91.81(4)	Sr2 ¹⁴	03	$Sr2^4$	100.84(15)
O1 ¹⁰	Sr2	Rh1	125.026(6)	Sr2 ³	03	Sr2 ¹	80.03(10)
O1 ⁸	Sr2	Rh1	148.13(7)	$Sr2^4$	03	Sr2 ¹	89.56(3)

 $^{1} 1/2 - X, -1/2 + Y, +Z; ^{2} - 1/4 + Y, 1/4 + X, 5/4 - Z; ^{3} - 3/4 + Y, 3/4 - X, 5/4 - Z; ^{4} + X, -1 + Y, +Z; ^{5} 1/4 + Y, 3/4 - X, 5/4 - Z; ^{6} 1 - X, 1/2 - Y, +Z; ^{7} 3/4 - Y, -1/4 + X, 5/4 - Z; ^{8} + X, 1 + Y, +Z; ^{9} 3/2 - X, 1/2 + Y, +Z; ^{10} 1 - X, 1 - Y, 1 - Z; ^{11} 1/2 - X, 1/2 + Y, +Z; ^{12} 3/4 - Y, 3/4 + X, 5/4 - Z; ^{8} + X, 1 + Y, +Z; ^{9} 3/2 - X, 1/2 + Y, +Z; ^{10} 1 - X, 1 - Y, 1 - Z; ^{11} 1/2 - X, 1/2 + Y, +Z; ^{12} 3/4 - Y, 3/4 + X, 5/4 - Z; ^{8} + X, 1 + Y, +Z; ^{9} 3/2 - X, 1/2 + Y, +Z; ^{10} 1 - X, 1 - Y, 1 - Z; ^{11} 1/2 - X, 1/2 + Y, +Z; ^{12} 3/4 - Y, 3/4 + X, 5/4 - Z; ^{13} 3/2 - X, -1/2 + Y, +Z; ^{14} - 1/4 + Y, -3/4 + X, 5/4 - Z; ^{10} - X, 1 - Y, 1 - Z; ^{11} 1/2 - X, 1/2 + Y, +Z; ^{10} - X$

Table 6 Atomic Occupancy for Sr2RhO4.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
Sr2	1.008(4)	01	1.03(2)	O3	1.035(18)

Experimental

Single crystals of O_4 RhSr₂ [Sr2RhO4] were [Grown by submitter by optical floating zone]. A suitable crystal was selected and [Mounted on thread] on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 296.15 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

2. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2013). in preparation.

3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of [Sr2RhO4]

Crystal Data for $O_4 \text{RhSr}_2$ (*M* = 342.15): tetragonal, space group I4₁/acd (no. 142), *a* = 5.4417(5) Å, *c* = 25.752(2) Å, *V* = 762.58(16) Å³, *Z* = 1, *T* = 296.15 K, $\mu(\text{MoK}\alpha) = 4.002 \text{ mm}^{-1}$, *Dcalc* = 0.745 g/mm³, 11354 reflections measured (6.328 $\leq 2\Theta \leq 90.598$), 807 unique ($R_{\text{int}} = 0.0589$, $R_{\text{sigma}} = 0.0265$) which were used in all calculations. The final R_1 was 0.0416 (I > 2 σ (I)) and *wR*₂ was 0.0769 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

```
Details:

1. Others

Fixed U12: Rh1(0)

Fixed U13: Rh1(0) Sr2(0) 01(0)

Fixed U23: Rh1(0) Sr2(0) 01(0)

Fixed X: Rh1(0.5) Sr2(0.5) 01(0.5)

Fixed Y: Rh1(0.25) Sr2(0.75) 01(0.25)

Fixed Z: Rh1(0.625) 03(0.625)
```

This report has been created with Olex2, compiled on 2014.03.20 svn.r2914 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

B.2 Low temperature measurements

Sr2RhO4LT_0m

le	1 Crystal data and structure	refinement for Sr2RhO4	
	Identification code	Sr2RhO4LT_0m	
	Empirical formula	Sr ₂ RhO ₄	
	Formula weight	2750.25	
	Temperature/K	100	
	Crystal system	tetragonal	
	Space group	I4 ₁ /acd	
	a/Å	5.4311(3)	
	b/Å	5.4311	
	c/Å	25.7530(14)	
	$\alpha/^{\circ}$	90	
	β/°	90	
	$\gamma/^{\circ}$	90	
	Volume/Å ³	759.63(6)	14
	Z	1	
	$ ho_{calc} mg/mm^3$	6.0117	
	m/mm ⁻¹	32.248	
	F(000)	1197.4	
	Crystal size/mm ³	$0.481 \times 0.364 \times 0.096$	
	Radiation	Mo K α (λ = 0.71073)	
	2Θ range for data collection	6.32 to 90.64°	
	Index ranges	$\textbf{-10} \le h \le 10, \textbf{-10} \le k \le 10, $	$-51 \le l \le 51$
	Reflections collected	11321	
	Independent reflections	$805 [R_{int} = 0.0550, R_{sigma}]$	= 0.0252]
	Data/restraints/parameters	805/0/21	
	Goodness-of-fit on F ²	1.179	
	Final R indexes [I>= 2σ (I)]	$R_1 = 0.0393, wR_2 = 0.063$	1
	Final R indexes [all data]	$R_1 = 0.0685, wR_2 = 0.078$	4
	Largest diff. peak/hole / e Å-	³ 4.28/-5.17	

Tab

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for Sr2RhO4LT_0m. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	У	z	U(eq)
Rh1	5000	2500	6250	1.92(11)
Sr2	5000	7500	5508.07(13)	3.22(11)
01	5000	2500	5451.1(11)	5.3(7)
03	2981(5)	5481(5)	6250	4.7(6)

Table 3 Anisotropic Displacement Parameters (Å²×10³) for Sr2RhO4LT_0m. The Anisotropic displacement factor exponent takes the f $-2\pi^{2}[h^{2}a^{*2}U_{11}+2hka^{*}b^{*}U_{12}+...].$

Atom
$$U_{11}$$
 U_{22} U_{33} U_{12} U_{13} U_{23}

Rh1	1.86(12)	1.86(12)	2.05(15)	-0	-0	0
Sr2	4.0(5)	3.2(5)	2.43(14)	-0.8(2)	-0	0
01	12(4)	0(3)	3.3(9)	0.4(17)	-0	0
03	3.4(8)	3.4(8)	7.2(12)	0.0(9)	-0.5(14)	0.5(14)

Table 4 Bond Lengths for Sr2RhO4LT_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Rh1	Sr2 ¹	3.3204(2)	Rh1	O3 ⁸	1.9555(7)
Rh1	Sr2 ²	3.3204(2)	Rh1	03	1.9555(7)
Rh1	Sr2 ³	3.3204(2)	Sr2	01	2.71951(16)
Rh1	Sr2 ⁴	3.3204(2)	Sr2	O1 ⁹	2.71951(16)
Rh1	Sr2 ⁵	3.3204(2)	Sr2	O1 ¹⁰	2.7195(2)
Rh1	Sr2 ⁶	3.3204(2)	Sr2	O1 ¹¹	2.7195(2)
Rh1	Sr2 ⁷	3.3204(2)	Sr2	O1 ¹²	2.470(3)
Rh1	Sr2	3.3204(2)	Sr2	O3 ¹³	2.982(3)
Rh1	01	2.057(3)	Sr2	03	2.461(2)
Rh1	O1 ⁴	2.057(3)	Sr2	O3 ¹⁴	2.982(3)
Rh1	O3 ⁴	1.9555(7)	Sr2	O3 ¹⁵	2.461(2)
Rh1	O3 ¹	1.9555(7)			

 $^{1}_{1/2-X,-1/2+Y,+Z;} ^{2}_{+X,-1+Y,+Z;} ^{3}_{-3/4+Y,3/4-X,5/4-Z;} ^{4}_{-1/4+Y,3/4-X,5/4-Z;} ^{5}_{-1/4+Y,1/4+X,5/4-Z;} ^{6}_{-3/2-X,-1/2+Y,+Z;} ^{7}_{-1/4+Y,-3/4+X,5/4-Z;} ^{8}_{-5/4-Y,1/4-X,5/4-Z;} ^{9}_{+X,1+Y,+Z;} ^{10}_{-3/2-X,1/2+Y,+Z;} ^{11}_{-1/2-X,1/2+Y,+Z;} ^{10}_{-1/2+Y,+Z;} ^{10}$

Atom	Atom	Atom	 Angle/°	Atom	Atom	Atom	Angle/°
a	DL 1	~ -?	Angic/	Atom	G.2	Atom	
Sr2 ⁺	KII	Sr2-	109./39(10)	01.5	Sr2	Rhl	38.22(6)
$Sr2^3$	Rh1	$\mathrm{Sr2}^2$	109.337(5)	01^{14}	Sr2	Rh1 ⁹	38.22(6)
$Sr2^4$	Rh1	Sr2 ²	180.0	01	Sr2	$Rh1^{10}$	91.78(4)
Sr2 ⁵	Rh1	Sr2 ⁶	109.337(5)	O1 ¹⁵	Sr2	Rh1 ¹²	125.130(5)
$\mathrm{Sr2}^7$	Rh1	Sr2 ⁶	70.663(5)	O1 ¹⁵	Sr2	Rh1 ¹⁰	125.130(5)
Sr2 ³	Rh1	Sr2 ⁷	109.739(10)	O1 ¹⁶	Sr2	Rh1 ¹¹	38.22(6)
Sr2 ³	Rh1	Sr2	70.261(10)	O1 ¹⁵	Sr2	Rh1 ⁹	125.130(5)
Sr2 ⁵	Rh1	Sr2 ²	70.663(5)	O1 ¹⁵	Sr2	Rh1 ¹¹	125.130(5)
Sr2 ³	Rh1	$Sr2^1$	109.337(5)	O1 ¹⁶	Sr2	Rh1 ¹⁰	91.78(4)
Sr2 ³	Rh1	Sr2 ⁶	70.663(5)	01	Sr2	Rh1 ⁹	91.78(4)
Sr2 ³	Rh1	Sr2 ⁵	180.0	01	Sr2	Rh1 ¹²	38.22(6)
Sr2	Rh1	Sr2 ⁵	109.739(10)	O1 ¹⁶	Sr2	Rh1 ⁹	91.78(4)
$\mathrm{Sr2}^4$	Rh1	$Sr2^7$	70.663(5)	O1 ¹⁶	Sr2	Rh1 ¹²	147.96(6)
Sr2 ⁴	Rh1	Sr2 ⁵	109.337(5)	01	Sr2	Rh1 ¹¹	147.96(6)
Sr2 ⁷	Rh1	Sr2 ⁵	70.261(10)	O1 ¹⁴	Sr2	Rh1 ¹²	91.78(4)
Sr2 ⁷	Rh1	Sr2 ²	109.337(5)	O1 ¹⁴	Sr2	Rh1 ¹⁰	147.96(6)
Sr2	Rh1	Sr2 ²	70.663(5)	O1 ¹³	Sr2	Rh1 ¹²	91.78(4)
Sr2	Rh1	Sr2 ¹	70.663(5)	O1 ¹³	Sr2	Rh1 ¹¹	91.78(4)
Sr2 ⁷	Rh1	Sr2 ¹	109.337(5)	O1 ¹³	Sr2	Rh1 ⁹	147.96(6)
Sr2 ⁴	Rh1	Sr2 ¹	70.261(10)	O1 ¹⁴	Sr2	Rh1 ¹¹	91.78(4)
	$\begin{array}{c} {\rm Atom} \\ {\rm Sr2}^1 \\ {\rm Sr2}^3 \\ {\rm Sr2}^4 \\ {\rm Sr2}^5 \\ {\rm Sr2}^7 \\ {\rm Sr2}^3 \\ {\rm Sr2}^4 \\ {\rm Sr2}^7 \\ {\rm Sr2}^7 \\ {\rm Sr2} \\ {\rm Sr2} \\ {\rm Sr2}^7 \\ {\rm S$	Atom Atom $Sr2^1$ Rh1 $Sr2^4$ Rh1 $Sr2^5$ Rh1 $Sr2^7$ Rh1 $Sr2^7$ Rh1 $Sr2^7$ Rh1 $Sr2^7$ Rh1 $Sr2^3$ Rh1 $Sr2^3$ Rh1 $Sr2^3$ Rh1 $Sr2^3$ Rh1 $Sr2^3$ Rh1 $Sr2^4$ Rh1 $Sr2^4$ Rh1 $Sr2^7$ Rh1 $Sr2^7$ Rh1 $Sr2^7$ Rh1 $Sr2^7$ Rh1 $Sr2^7$ Rh1 $Sr2^7$ Rh1 $Sr2$ Rh1 <tr td=""></tr>	AtomAtomAtom $Sr2^1$ Rh1 $Sr2^2$ $Sr2^3$ Rh1 $Sr2^2$ $Sr2^4$ Rh1 $Sr2^2$ $Sr2^5$ Rh1 $Sr2^6$ $Sr2^7$ Rh1 $Sr2^6$ $Sr2^3$ Rh1 $Sr2^7$ $Sr2^3$ Rh1 $Sr2^7$ $Sr2^3$ Rh1 $Sr2^2$ $Sr2^3$ Rh1 $Sr2^1$ $Sr2^3$ Rh1 $Sr2^1$ $Sr2^3$ Rh1 $Sr2^6$ $Sr2^3$ Rh1 $Sr2^6$ $Sr2^3$ Rh1 $Sr2^5$ $Sr2$ Rh1 $Sr2^5$ $Sr2^4$ Rh1 $Sr2^7$ $Sr2^7$ Rh1 $Sr2^2$ $Sr2$ Rh1 $Sr2^2$ $Sr2$ Rh1 $Sr2^2$ $Sr2$ Rh1 $Sr2^2$ $Sr2$ Rh1 $Sr2^1$ $Sr2^7$ Rh1 $Sr2^1$	AtomAtomAtomAngle/° $Sr2^1$ Rh1 $Sr2^2$ $109.739(10)$ $Sr2^3$ Rh1 $Sr2^2$ $109.337(5)$ $Sr2^4$ Rh1 $Sr2^2$ $109.337(5)$ $Sr2^4$ Rh1 $Sr2^2$ 180.0 $Sr2^5$ Rh1 $Sr2^6$ $109.337(5)$ $Sr2^7$ Rh1 $Sr2^6$ $70.663(5)$ $Sr2^3$ Rh1 $Sr2^7$ $109.739(10)$ $Sr2^3$ Rh1 $Sr2^7$ $109.739(10)$ $Sr2^3$ Rh1 $Sr2^2$ $70.261(10)$ $Sr2^3$ Rh1 $Sr2^2$ $70.663(5)$ $Sr2^3$ Rh1 $Sr2^6$ $70.663(5)$ $Sr2^3$ Rh1 $Sr2^6$ $109.337(5)$ $Sr2^4$ Rh1 $Sr2^7$ $109.337(5)$ $Sr2^7$ Rh1 $Sr2^7$ $70.663(5)$ $Sr2^7$ Rh1 $Sr2^2$ $109.337(5)$ $Sr2^7$ Rh1 $Sr2^2$ $70.663(5)$ $Sr2^7$ Rh1 $Sr2^1$ $109.337(5)$ $Sr2^7$ Rh1 $Sr2^2$ $70.663(5)$ $Sr2^7$ Rh1 $Sr2^1$ $70.261(10)$	AtomAtomAtomAngle/°Atom $Sr2^1$ Rh1 $Sr2^2$ $109.739(10)$ $O1^{13}$ $Sr2^3$ Rh1 $Sr2^2$ $109.337(5)$ $O1^{14}$ $Sr2^4$ Rh1 $Sr2^2$ $109.337(5)$ $O1$ $Sr2^5$ Rh1 $Sr2^6$ $109.337(5)$ $O1^{15}$ $Sr2^7$ Rh1 $Sr2^6$ $70.663(5)$ $O1^{15}$ $Sr2^7$ Rh1 $Sr2^6$ $70.663(5)$ $O1^{16}$ $Sr2^3$ Rh1 $Sr2^7$ $109.739(10)$ $O1^{16}$ $Sr2^3$ Rh1 $Sr2^2$ $70.663(5)$ $O1^{15}$ $Sr2^3$ Rh1 $Sr2^2$ $70.663(5)$ $O1^{16}$ $Sr2^3$ Rh1 $Sr2^6$ $70.663(5)$ $O1$ $Sr2^3$ Rh1 $Sr2^6$ $70.663(5)$ $O1$ $Sr2^3$ Rh1 $Sr2^5$ $109.739(10)$ $O1^{16}$ $Sr2^3$ Rh1 $Sr2^5$ $109.739(10)$ $O1^{16}$ $Sr2^4$ Rh1 $Sr2^7$ $70.663(5)$ $O1$ $Sr2^4$ Rh1 $Sr2^5$ $109.337(5)$ $O1^{14}$ $Sr2^7$ Rh1 $Sr2^2$ $70.663(5)$ $O1^{13}$ $Sr2^7$ Rh1 $Sr2^1$ $70.663(5)$ $O1^{13}$ $Sr2^7$ Rh1 $Sr2^1$ $70.663(5)$ $O1^{13}$ $Sr2^7$ Rh1 $Sr2^1$ $70.663(5)$ $O1^{13}$ $Sr2^4$ Rh1 $Sr2^1$ $70.261(10)$ $O1^{14}$	AtomAtomAtomAngle/°AtomAtom $Sr2^1$ Rh1 $Sr2^2$ $109.739(10)$ $O1^{13}$ $Sr2$ $Sr2^3$ Rh1 $Sr2^2$ $109.337(5)$ $O1^{14}$ $Sr2$ $Sr2^4$ Rh1 $Sr2^2$ 180.0 $O1$ $Sr2$ $Sr2^5$ Rh1 $Sr2^6$ $109.337(5)$ $O1^{15}$ $Sr2$ $Sr2^7$ Rh1 $Sr2^6$ $109.337(5)$ $O1^{15}$ $Sr2$ $Sr2^7$ Rh1 $Sr2^6$ $70.663(5)$ $O1^{15}$ $Sr2$ $Sr2^3$ Rh1 $Sr2^7$ $109.739(10)$ $O1^{16}$ $Sr2$ $Sr2^3$ Rh1 $Sr2^7$ $70.261(10)$ $O1^{15}$ $Sr2$ $Sr2^3$ Rh1 $Sr2^7$ $70.663(5)$ $O1^{15}$ $Sr2$ $Sr2^3$ Rh1 $Sr2^1$ $109.337(5)$ $O1^{16}$ $Sr2$ $Sr2^3$ Rh1 $Sr2^5$ $109.739(10)$ $O1^{16}$ $Sr2$ $Sr2^3$ Rh1 $Sr2^5$ $109.739(10)$ $O1^{16}$ $Sr2$ $Sr2^3$ Rh1 $Sr2^5$ $109.739(10)$ $O1^{16}$ $Sr2$ $Sr2^4$ Rh1 $Sr2^5$ $109.739(10)$ $O1^{16}$ $Sr2$ $Sr2^4$ Rh1 $Sr2^5$ $109.337(5)$ $O1$ $Sr2$ $Sr2^4$ Rh1 $Sr2^5$ $109.337(5)$ $O1^{14}$ $Sr2$ $Sr2^7$ Rh1 $Sr2^2$ $109.337(5)$ $O1^{14}$ $Sr2$ $Sr2^7$ Rh1 $Sr2^2$ $70.663(5)$ $O1^{13}$ $Sr2$ $Sr2^7$ Rh1 $Sr2^1$ <td< td=""><td>$\begin{array}{c ccccccccccccccccccccccccccccccccccc$</td></td<>	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Table 5 Bond Angles for Sr2RhO4LT_0m.

Sr2 ¹	Rh1	Sr2 ⁶	180.0	O1 ¹⁴	Sr2	O1 ¹⁵	86.91(6)
Sr2 ⁴	Rh1	Sr2 ⁶	109.739(10)	O1 ¹⁴	Sr2	O1 ¹⁶	89.833(7)
Sr2	Rh1	Sr2 ⁶	109.337(5)	O1 ¹⁴	Sr2	O1 ¹³	173.82(13)
Sr2 ⁴	Rh1	Sr2	109.337(5)	01	Sr2	O1 ¹³	89.833(7)
014	Rh1	Sr2 ²	125.130(5)	01	Sr2	O1 ¹⁵	86.91(6)
01 ⁴	Rh1	Sr2 ⁶	54.870(5)	01	Sr2	O1 ¹⁶	173.82(13)
O1 ⁴	Rh1	Sr2 ⁷	54.870(5)	O3 ¹⁷	Sr2	Rh1 ¹²	35.640(6)
01	Rh1	Sr2 ¹	54.870(5)	03	Sr2	Rh1 ¹⁰	85.27(6)
01	Rh1	Sr2	54.870(5)	O3 ¹⁷	Sr2	Rh1 ¹¹	94.32(4)
01 ⁴	Rh1	Sr2 ⁵	125.130(5)	O3 ¹⁰	Sr2	Rh1 ¹⁰	35.784(11)
01 ⁴	Rh1	Sr2	125.130(5)	03	Sr2	Rh1 ¹²	35.784(11)
01	Rh1	Sr2 ²	54.870(5)	O3 ¹¹	Sr2	Rh1 ¹⁰	94.32(4)
01	Rh1	Sr2 ⁷	125.130(5)	O3 ¹⁰	Sr2	Rh1 ¹²	85.27(6)
01	Rh1	Sr2 ⁶	125.130(5)	O3 ¹¹	Sr2	Rh1 ¹¹	35.640(6)
01 ⁴	Rh1	Sr2 ⁴	54.870(5)	03	Sr2	Rh1 ⁹	35.784(11)
01	Rh1	Sr2 ³	125.130(5)	O3 ¹⁰	Sr2	Rh1 ⁹	85.27(6)
01 ⁴	Rh1	Sr2 ³	54.870(5)	O3 ¹¹	Sr2	Rh1 ⁹	35.640(6)
01	Rh1	Sr2 ⁵	54.870(5)	03	Sr2	$Rh1^{11}$	85.27(6)
01 ⁴	Rh1	Sr2 ¹	125.130(5)	O3 ¹¹	Sr2	Rh1 ¹²	94.32(4)
01	Rh1	Sr2 ⁴	125.130(5)	O3 ¹⁰	Sr2	Rh1 ¹¹	35.784(11)
01	Rh1	01 ⁴	180.0	O3 ¹⁷	Sr2	Rh1 ⁹	94.32(4)
0.03^{2}	Rh1	Sr2 ⁶	47.37(7)	O3 ¹⁷	Sr2	Rh1 ¹⁰	35.640(6)
0.03^{2}	Rh1	Sr2	117.29(8)	03	Sr2	01	66.23(7)
03	Rh1	Sr2 ²	62.71(8)	03	Sr2	O1 ¹⁴	66.23(7)
03	Rh1	Sr2 ⁵	132.63(7)	O3 ¹⁰	Sr2	O1 ¹⁵	140.94(7)
03	Rh1	Sr2 ⁶	62.71(8)	O3 ¹¹	Sr2	O1 ¹⁶	59.50(6)
O3 ⁴	Rh1	Sr2 ¹	47.37(7)	O3 ¹¹	Sr2	O1 ¹⁵	129.84(5)
O3 ⁴	Rh1	$\mathrm{Sr2}^2$	132.63(7)	O3 ¹⁰	Sr2	O1 ¹³	66.23(7)
O3 ⁴	Rh1	Sr2 ⁴	47.37(7)	O3 ¹¹	Sr2	01	125.22(5)
O3 ⁸	Rh1	Sr2 ²	117.29(8)	O3 ¹¹	Sr2	O1 ¹³	125.22(5)
O3 ⁸	Rh1	Sr2 ³	132.63(7)	O3 ¹⁷	Sr2	01	59.50(6)
03	Rh1	$\mathrm{Sr2}^4$	117.29(8)	O3 ¹⁰	Sr2	O1 ¹⁴	119.13(7)
O3 ⁸	Rh1	Sr2 ⁴	62.71(8)	O3 ¹⁰	Sr2	01	119.13(7)
O3 ²	Rh1	Sr2 ²	47.37(7)	03	Sr2	O1 ¹³	119.13(7)
O3 ⁴	Rh1	Sr2 ⁶	132.63(7)	O3 ¹⁷	Sr2	O1 ¹⁴	125.22(5)
O3 ⁴	Rh1	Sr2 ⁵	117.29(8)	O3 ¹⁷	Sr2	O1 ¹³	59.50(6)
O3 ²	Rh1	Sr2 ⁵	62.71(8)	O3 ¹⁷	Sr2	O1 ¹⁶	125.22(5)
O3 ²	Rh1	Sr2 ¹	132.63(7)	03	Sr2	O1 ¹⁶	119.13(7)
O3 ⁸	Rh1	Sr2 ⁶	117.29(8)	03	Sr2	O1 ¹⁵	140.94(7)
O3 ⁸	Rh1	Sr2 ¹	62.71(8)	O3 ¹⁰	Sr2	O1 ¹⁶	66.23(7)
03	Rh1	Sr2	47.37(7)	O3 ¹⁷	Sr2	O1 ¹⁵	129.84(5)
O3 ⁸	Rh1	Sr2	132.63(7)	O3 ¹¹	Sr2	O1 ¹⁴	59.50(6)
O3 ²	Rh1	Sr2 ⁴	132.63(7)	O3	Sr2	O3 ¹¹	60.17(7)
O3 ⁸	Rh1	Sr2 ⁵	47.37(7)	O3 ¹⁷	Sr2	O3 ¹⁰	60.17(7)
O3 ⁴	Rh1	Sr2 ⁷	117.29(8)	O3 ¹⁷	Sr2	O3 ¹¹	100.32(9)
O3 ²	Rh1	Sr2 ⁷	62.71(8)	03	Sr2	O3 ¹⁰	78.11(13)
03	Rh1	Sr2 ¹	117.29(8)	Sr2 ¹	01	Rh1 ¹²	86.91(6)

$O3^2$	Rh1	Sr2 ³	117.29(8)	$\mathrm{Sr2}^2$	01	Rh1 ¹²	86.91(6)
O3 ⁴	Rh1	Sr2	62.71(8)	Sr2 ¹⁵	01	Rh1 ¹²	180.0
O3 ⁴	Rh1	Sr2 ³	62.71(8)	Sr2 ⁵	01	Rh1 ¹²	86.91(6)
03	Rh1	Sr2 ³	47.37(7)	Sr2	01	Rh1 ¹²	86.91(6)
O3	Rh1	Sr2 ⁷	132.63(7)	Sr2	01	Sr2 ⁵	173.82(13)
O3 ⁸	Rh1	Sr2 ⁷	47.37(7)	Sr2 ²	01	Sr2 ¹⁵	93.09(6)
O3 ²	Rh1	O1 ⁴	90.0	Sr2 ²	01	Sr2 ¹	173.82(13)
O3 ⁴	Rh1	01	90.0	Sr2	01	Sr2 ¹⁵	93.09(6)
O3 ⁴	Rh1	O1 ⁴	90.0	Sr2	01	Sr2 ¹	89.833(7)
O3 ⁸	Rh1	01	90.0	Sr2 ²	01	Sr2 ⁵	89.833(7)
O3 ²	Rh1	01	90.0	Rh1	03	Rh1 ¹⁴	158.2(2)
O3	Rh1	O1 ⁴	90.0	$Sr2^{12}$	03	Rh1	81.65(9)
03	Rh1	01	90.0	$Sr2^{12}$	03	Rh1 ¹⁴	81.65(9)
O3 ⁸	Rh1	O1 ⁴	90.0	Sr2	O3	Rh1	96.84(6)
O3 ⁸	Rh1	03	180.0	$\mathrm{Sr2}^{10}$	03	Rh1 ¹⁴	96.84(6)
O3 ⁴	Rh1	O3 ²	180.0	$\mathrm{Sr2}^{10}$	03	Rh1	96.84(6)
O3 ⁴	Rh1	03	90.00(8)	Sr2 ²	03	Rh1	81.65(9)
O3 ⁸	Rh1	O3 ²	90.00(8)	Sr2 ²	03	Rh1 ¹⁴	81.65(9)
O3	Rh1	O3 ²	90.00(6)	Sr2	03	Rh1 ¹⁴	96.84(6)
O3 ⁸	Rh1	O3 ⁴	90.00(9)	Sr2 ¹²	03	Sr2 ²	79.68(9)
Rh1 ⁹	Sr2	Rh1 ¹⁰	109.739(10)	Sr2	03	Sr2 ²	89.22(2)
Rh1 ⁹	Sr2	Rh1 ¹¹	70.663(5)	$Sr2^{12}$	03	Sr2 ¹⁰	89.22(2)
$Rh1^{12}$	Sr2	Rh1 ¹⁰	70.663(5)	Sr2	03	$\mathrm{Sr2}^{10}$	101.89(14)
$Rh1^{12}$	Sr2	Rh1 ¹¹	109.739(10)				

 $^{13}_{2-X,-1/2+Y,+Z;} ^{2}_{1/2-X,-1/2+Y,+Z;} ^{3}_{-1/4+Y,1/4+X,5/4-Z;} ^{4}_{1/4+Y,3/4-X,5/4-Z;} ^{5}_{+X,-1+Y,+Z;} ^{6}_{-3/4+Y,3/4-X,5/4-Z;} ^{7}_{-1/4+Y,-3/4+X,5/4-Z;} ^{8}_{5/4-Y,1/4-X,5/4-Z;} ^{9}_{1/4-Y,5/4-X,5/4-Z;} ^{10}_{5/4-Y,5/4-X,5/4-Z;} ^{10}_{-1/4+Y,-3/4+X,5/4-Z;} ^{10}_{-1/4+Y,-3$

Table 6 Atomic Occupancy for Sr2RhO4LT_0m.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
Sr2	1.004(4)	01	1.024(19)	O3	1.007(18)

Experimental

Single crystals of Sr_2RhO_4 [Sr2RhO4LT_0m] were [grown by submitter via optical floating zone]. A suitable crystal was selected and [mounted on thread] on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 100 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the olex2.refine [3] refinement package using Gauss-Newton minimisation.

- 1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
- 2. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2013). in preparation.
- 3. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2013). in preparation.

Crystal structure determination of [Sr2RhO4LT_0m]

Crystal Data for Sr₂RhO₄ (*M*=2750.25): tetragonal, space group I4₁/acd (no. 142), a = 5.4311(3) Å, c = 25.7530(14) Å, V = 759.63(6) Å³, Z = 1, T = 100 K, μ (Mo K α) = 32.248 mm⁻¹, *Dcalc* = 6.0117 g/mm³, 11321 reflections measured (6.32 $\leq 2\Theta \leq 90.64$), 805 unique ($R_{int} = 0.0550$, $R_{sigma} = 0.0252$) which were used in all calculations. The final R_1 was 0.0393 (I>=2u(I)) and wR_2 was 0.0784 (all data).

Refinement model description

Number of restraints - 0, number of constraints - 0. Details: N/A

This report has been created with Olex2, compiled on 2014.03.20 svn.r2914 for OlexSys. Please let us know if there are any errors or if you would like to have additional features

Appendix C

MATLAB Code

C.1 Code used to simulate Fermi liquid behavior

Contents

- Kevin Mortimer
- Variable definition
- Function definition
- Noise generation
- Calculation of 1/tau and Xi.
- Extracting R squared
- Plotting

Kevin Mortimer

```
% Simulations of fitting to Fermi Liquid Scaling
% Last modified May 18th, 2014
% COMMENT THESE OUT IF YOU WANT TO SAVE YOUR WORKSPACE
close all
clear all
```

Variable definition

filename = 'StrickerSim'; %Leading name of the file to be saved

```
fileappend =''; %Trailing name of the file to be saved
ColorArray = \{ [0 \ 0 \ 0 ], [1 \ 0 \ 0], [0 \ 1 \ 0], [0 \ 0 \ 1], 
        [1 \ 1 \ 0], [.5 \ .6 \ .7], [.8 \ .2 \ .6]\};
MaxFreq = 36; % in meV
MinFreq = 2; % in meV
FreqStep = 0.05; % in meV
FreqVec = MinFreq:FreqStep:MaxFreq;
MaxTemp = 40; % in Kelvin
MinTemp = 10; % in Kelvin
TempStep = 5; % in Kelvin
TempVec1 = MinTemp:TempStep:MaxTemp;
TempVec = TempVec1 * .086; % convert to meV
b = [2,3,4,5,6];
InverseTau = zeros(length(b),length(FreqVec),length(TempVec));
Xi = zeros(length(b),length(FreqVec),length(TempVec));
TempNames = cell(length(TempVec1),1);
```

Function definition

```
%This set of parameters generates data similar to Stricker,
%gives b=4, and also is Fermi liquid like.
\% TempCoef1 = 2;
% TempCoef2 = 0;
% TempScale1 = 0.8;
% TempScale2 = 0;
% FreqCoef1 = 2;
% FreqCoef2 = -4;
% FreqScale1 = .02;
\% FreqScale2 = 400;
% Offset = 10;
%This set of parameters generates data similar to Stricker
%and gives b=4 without Fermi liquid like scaling.
TempCoef1 = 1;
TempCoef2 = 0;
TempScale1 = 4;
```

```
TempScale2 = 0;
FreqCoef1 = 1;
FreqCoef2 = -4;
FreqScale1 = 1.0;
FreqScale2 = 500;
Offset = 10;
```

Noise generation

```
NoiseWeight = 5;
NoiseType = 'p';
if strcmpi(NoiseType,'White')||strcmpi(NoiseType,'w')
    NoiseType = 'white';
    ScalingLaw = 0;
elseif strcmp(NoiseType, 'Pink')||strcmpi(NoiseType,'p')
    %Intensity falls off by ten decibels (amplitude of sqrt(10))
    %every factor of 10 in frequency
    NoiseType = 'pink';
    ScalingLaw = (1/2);
elseif strcmp(NoiseType, 'Blue')||strcmpi(NoiseType,'b')
    %Intensity increases by 10 decibels every factor of 10 in
    %frequency
    NoiseType = 'blue';
    ScalingLaw = (-1/2);
elseif strcmp(NoiseType, 'Red')||strcmpi(NoiseType,'r')
    %Intensity falls off by 20 decibels (amplitude of (10))
    %every factor of 10 in frequency
    NoiseType = 'red';
    ScalingLaw = (1);
elseif strcmp(NoiseType,'Special')||strcmpi(NoiseType,'s')
    NoiseType = 'special';
    ScalingLaw = (.8);
end
ScalingVec = FreqVec.^(-ScalingLaw) * FreqVec(1)^(ScalingLaw);
ScalingMat = repmat(ScalingVec,length(TempVec),1);
NoiseVec = NoiseWeight*randn(length(FreqVec),length(TempVec))
```

.*ScalingMat';

Calculation of 1/tau and Xi.

```
for CurB = 1:length(b)
    for CurTemp = 1:length(TempVec)
        Xi(CurB, :, CurTemp) = FreqVec.^2
    + b(CurB)*pi*pi*TempVec(CurTemp)^2;
        InverseTau(CurB, :, CurTemp) = Offset
    + FreqScale1.*FreqVec.^FreqCoef1
            + FreqScale2.*FreqVec.^FreqCoef2
            + TempScale1*TempVec(CurTemp)^TempCoef1
            + TempScale2*TempVec(CurTemp)^TempCoef2
            + NoiseVec(:,CurTemp)';
    end
end
InverseTau = abs(InverseTau);
```

Extracting R squared

Plotting

```
for CurPlot = 1:length(b)
    %figure(CurPlot)
    figure('Position', [100,100,900,600])
    for CurTemp = 1:length(TempVec)
        plot(Xi(CurPlot,:,CurTemp),InverseTau(CurPlot,
:,CurTemp),
          'LineStyle', 'none', 'Marker', '.',
'Color',ColorArray{CurTemp}');
        hold on
        TempNames{CurTemp,1} = sprintf('T=%0.3g K',
TempVec1(CurTemp));
    end
    hold off
    xlabel(strcat('\xi(b) in meV^{2}',
sprintf(',b=%0.3g, R^2 = %0.4g',
                b(CurPlot),RSq(CurPlot))),'FontSize',11)
    ylabel('1/{\tau} in meV', 'FontSize',11)
    legend(TempNames,4);
    title(sprintf('1/Tau = %0.3g + %0.3g*Freq^{%0.3g}
        + %0.3g*Freq^{%0.3g} + %0.3g*Temp^{%0.3g}
        + %0.3g*Temp^{%0.3g} + %0.3g meV of %s noise',Offset,
FreqScale1,FreqCoef1,FreqScale2,FreqCoef2,TempScale1,
TempCoef1,TempScale2,TempCoef2,NoiseWeight,NoiseType),
'FontSize',11);
    set(gca, 'FontSize',11);
ylim([0 10*ceil((max(max(max(InverseTau))))/10)]);
    saveas(CurPlot,strcat(filename,int2str(CurPlot),fileappend),
       'png');
end
```