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Neutron diffraction and magnetisation studies of Sr_2RuO_4 below 2 K

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Abstract

High resolution neutron powder diffraction and magnetisation measurements have been carried out on the superconductor, Sr_2RuO_4 . The powder diffraction data has been refined at high and low temperatures to obtain lattice parameters below the superconducting transition temperature (1.15 K) and at elevated temperatures where Sr_2RuO_4 is used as a substrate for the deposition of $\text{YBa}_2\text{Cu}_3\text{O}_7$ thin films. No evidence has been found for any lattice distortions between 100 mK and 2 K in Sr_2RuO_4 . Magnetisation measurements between 0.7 K and room temperature has indicated the onset of superconductivity at 1.15 K.

1. Introduction

Sr_2RuO_4 crystallises in the K_2NiF_4 structure, similar to the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ superconductor and recently it has been shown to be superconducting below 0.93 K [1]. In the normal state, Sr_2RuO_4 shows metallic conductivity along the ab plane ($\sim 10^{-6} \Omega \text{ cm}$) and a lower conductivity ($\sim 10^{-3} \Omega \text{ cm}$) along the c -axis [2]. The electronic anisotropy, characterised by the ratio of the resistivity parallel to the plane and perpendicular to it (ρ_c/ρ_{ab}), exhibits a crossover from non-metallic to metallic behaviour at approximately 130 K [1].

Sr_2RuO_4 is thought to be the only K_2NiF_4 -type perovskite to exhibit superconductivity without the

presence of copper ions. It could therefore give us a unique insight into the role that copper plays in the high T_c superconductors. Ruthenium is a second-row transition metal with spin, $S = 1$, as opposed to the first row Cu ions ($S = 1/2$) in the cuprates. Other compounds isostructural to the cuprate superconductors, such as La_2NiO_4 (first-row transition metal, $S = 1$) [3] and Sr_2RhO_4 (second-row transition metal, $S = 1/2$) [1] are not superconducting.

Another important difference between the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and Sr_2RuO_4 superconductors is that the electronic states at the Fermi level is induced by hole doping (either with excess oxygen or trivalent ions substituted on the lanthanum site) in the high T_c compounds, whereas strontium ruthenate is superconducting without the need for any doping. Unfortunately the superconducting transition temperature is approximately 40 times smaller in the ruthenates than the doped cuprates which makes it difficult to

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investigate its physical properties and impractical for applications.

Sr_2RuO_4 has been known for many years and it has been the topic of many studies due to its K_2NiF_4 crystal structure [2,4,5]. There has been renewed interest in this compound, firstly, due to its potential as a metallic substrate for high T_c thin films and more recently because of its superconducting properties. Neumeier et al. [6] in their investigations of the magnetic properties of Sr_2RuO_4 find that SrRuO_3 occurs as an impurity phase in the samples and could be detected in magnetic susceptibility measurements at its Curie temperature ($T_c = 160$ K) [7], even in samples that showed no impurities in neutron and X-ray diffraction studies. Neumeier et al. [6] also reported that Sr_2RuO_4 appears to exhibit weak anti-ferromagnetic order below 45 K from magnetic susceptibility measurements.

In an earlier study, we reported the lattice parameters of Sr_2RuO_4 between 5 K and 973 K [4] and showed that the crystal structure remains tetragonal (space group $I4/mmm$) between 5 K and 973 K and that the good lattice match between Sr_2RuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_7$ at these temperatures makes it suitable as a substrate for epitaxial growth of high T_c thin films. In this paper we extend our investigations to lower temperatures and present results of the temperature dependence of the lattice parameters of impurity free Sr_2RuO_4 down to 110 mK, well below the superconducting transition temperature. Magnetic susceptibility results from 700 mK up to 250 K are also presented in this paper.

2. Experimental details

The polycrystalline sample was prepared by reacting, in air, appropriate proportions of SrCO_3 (99.99%) and Ru metal (99.99%) for 40 hours at 1200°C with several intermittent grindings to ensure a complete reaction, before sintering at 1300°C . The sample was characterised by X-ray powder diffraction, resistivity and susceptibility measurements prior to the neutron experiment. The neutron powder diffraction experiments were carried out on the high resolution powder diffractometer (HRPD) at the pulsed neutron source, ISIS. The samples were enclosed in a vanadium container and then placed in a

dilution refrigerator, helium bath cryostat or furnace to carry out experiments between 110 mK and 973 K. The refinement of the Sr_2RuO_4 data was carried out assuming the tetragonal K_2NiF_4 -type structure of space groups $I4/mmm$ and $P4_2/nm$ and the orthorhombic Cmca structure using the Rietveld method. This method compares the complete calculated powder diffraction pattern with the one observed, and optimises the degree of fit by adjusting

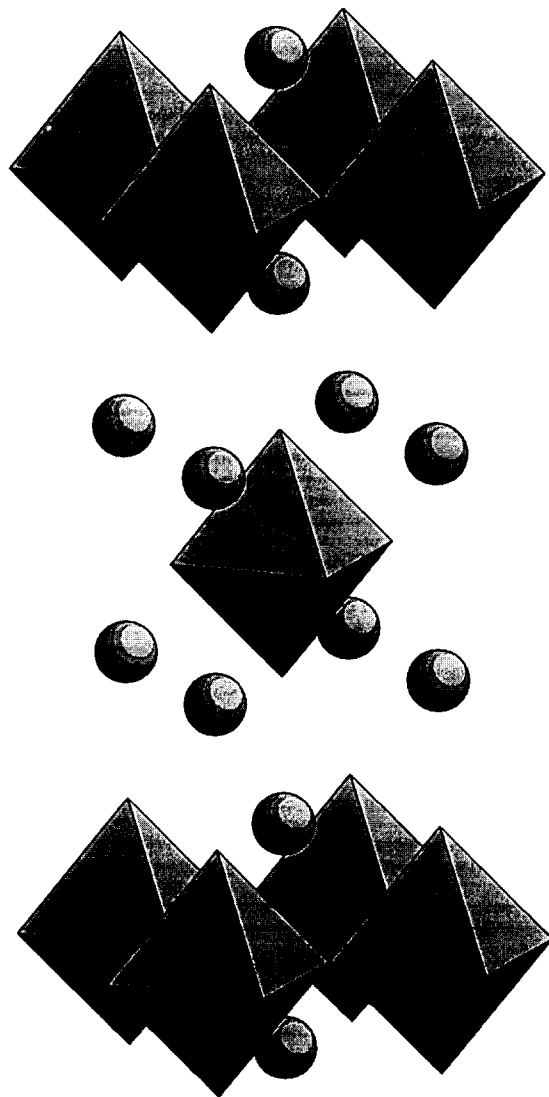


Fig. 1. Schematic representation of the tetragonal structures of Sr_2RuO_4 , K_2NiF_4 ($I4/mmm$). The octahedral coordination of Ru ion and the Sr sites (balls) are shown.

the various structural parameters by non-linear least square fitting.

Low temperature ($T < 1.5$ K) magnetic susceptibility measurements were carried out in a De Haas–Van Alphen instrument. A polycrystalline sample was placed in one of a pair of balanced coils and a phase sensitive detector (p.s.d) is used to measure the signal at twice the fundamental frequency (fundamental = 18 Hz) in order to reduce the amount of noise. Between 20 and 250 K the susceptibility was measured by the mutual inductance method within a helium bath cryostat. An excitation field of 10 Oe was supplied from the primary coil and a

p.s.d. was used to detect the signal in the secondary coils at a frequency of 114 Hz.

3. Results and discussion

The room temperature tetragonal unit cell of Sr_2RuO_4 with space group $I4/mmm$, is shown in Fig. 1. The strontium atom lies approximately in the basal plane of a quadratic pyramid of five oxygen atoms and the ruthenium atoms have a distorted octahedral coordination. The atomic arrangement is similar to that of La_2CuO_4 and its Sr and Ba based

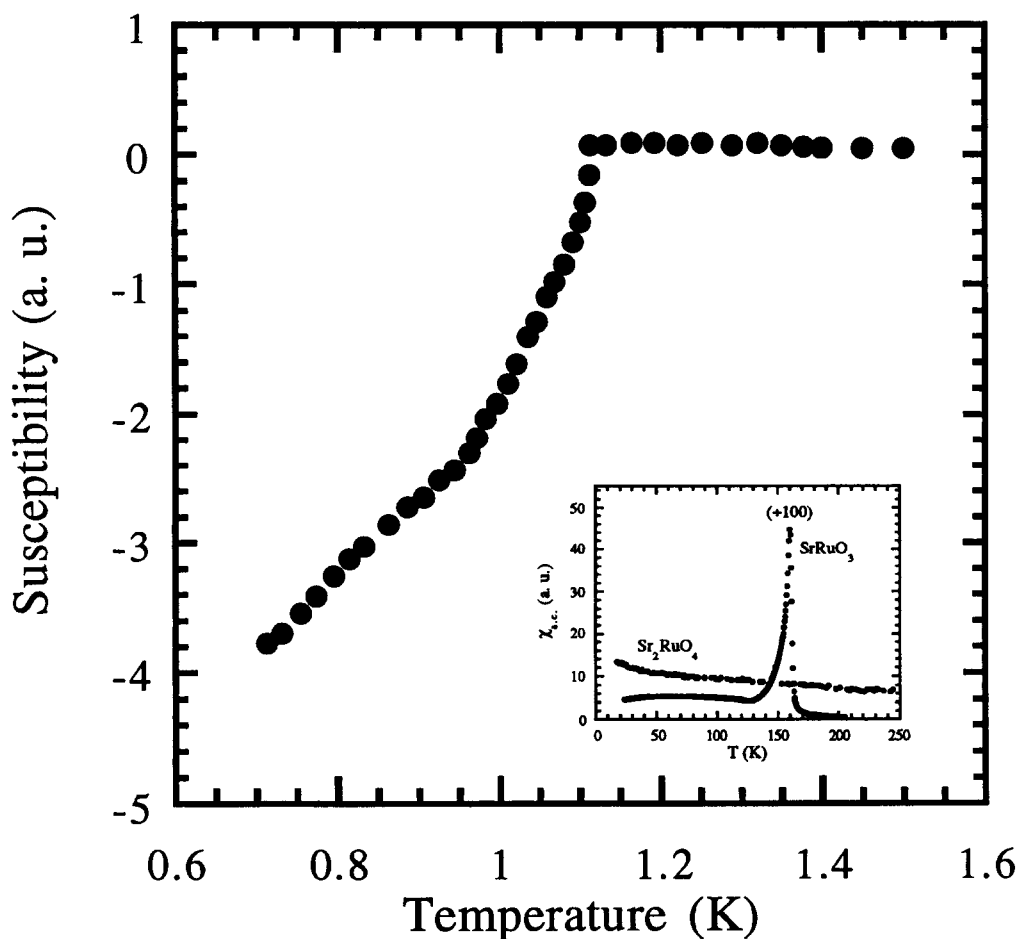


Fig. 2. Magnetic susceptibility vs. temperature of Sr_2RuO_4 . The inset shows the high temperature data of Sr_2RuO_4 and the signal expected from any SrRuO_3 impurities at 160 K.

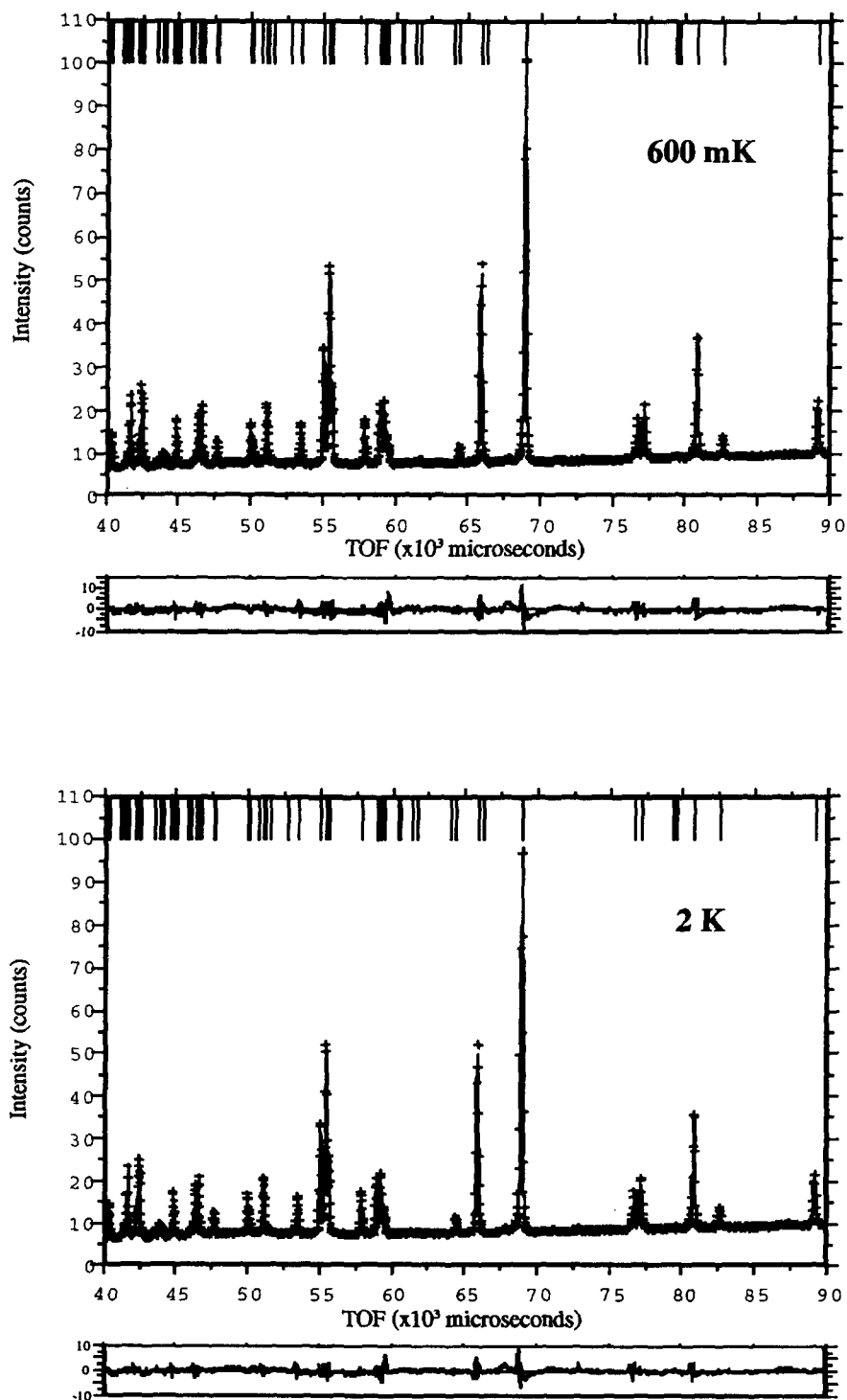


Fig. 3. Rietveld refinement plots of Sr_2RuO_4 at 600 mK and 2 K. The tick marks indicate the positions of the allowed Bragg reflections for the space group $I4/mmm$ and the lower curve shows the difference between the observed and calculated intensities.

derivatives except that the deformity in the octahedron is considerably less.

Fig. 2 shows the magnetic susceptibility of Sr_2RuO_4 . The onset of superconductivity has been observed at 1.15 K. Maeno et al. report the observation of a diamagnetic transition in polycrystalline Sr_2RuO_4 at ~ 1 K and a T_c of 0.93 K in single crystal Sr_2RuO_4 [1]. Similar to Maeno et al. we were unable to observe a superconducting transition in resistivity measurements on polycrystalline samples at this temperature. Zero resistance has however been observed by Maeno et al. only in single crystal samples of Sr_2RuO_4 [1]. To rule out the possibility of the presence of small amounts of SrRuO_3 impurity in our samples, we have also measured the a.c. susceptibility of SrRuO_3 and the inset in Fig. 2 shows the signal from a.c. susceptibility measurements carried out on similar masses of polycrystalline Sr_2RuO_4 and SrRuO_3 . There is no indication of any SrRuO_3 impurity in our samples of Sr_2RuO_4 . Neumeier et al. [6] reported the observation of an anomaly at 45 K in their magnetic susceptibility

measurements of Sr_2RuO_4 from which they deduced the onset of a weak antiferromagnetic state. In our sample, there is no indication of any anomaly in the a.c. susceptibility at 45 K or at any other temperature to indicate the onset of antiferromagnetic ordering.

New diffraction data collected at 110 mK, 600 mK and 2 K and high temperature data from our earlier study [4] are presented in this paper. Rietveld analysis of the Sr_2RuO_4 time-of-flight neutron diffraction data was carried out between $0.76 \text{ \AA} < \lambda < 2.24 \text{ \AA}$, which includes approximately 250 observed reflections. The best agreements between the calculated intensities and the experimental data, at all temperatures, was achieved by fitting the data to the $I4/mmm$ space group. The results of the refinement on either side of the superconducting transition temperature (0.6 and 2 K) are shown in Fig. 3 and the crystal parameters determined at other temperatures are summarised in Table 1. The tick marks indicate the positions of the allowed Bragg reflections in space group $I4/mmm$ and the difference between the calculated and observed intensities are shown in

Table 1

The results from Rietveld analysis of Sr_2RuO_4 . The atomic positions and the isotropic B factors are reported. The weighted (R_{wp}) and expected (R_e) R -factors [8] indicating the goodness of the fits are also shown

Atom	x	y	z	$B(1, 1)$	$B(2, 2)$	$B(3, 3)$
$T(\text{K}) = 110 \text{ mK } a = 3.86282(1) \text{ \AA}$				$c = 12.72073(2) \text{ \AA}$		
Sr	0	0	0.35332(4)	0.02(1)	0.02(1)	0.02(1)
Ru	0	0	0	0.04(2)	0.04(2)	0.01(1)
O(1)	0	0	0.16154(6)	0.07(2)	0.07(2)	0.02(1)
O(2)	0	1/2	0	0.04(1)	0.04(1)	0.01(1)
$R_{wp} = 4.7\%$			$R_e = 4.4\%$			
$T(\text{K}) = 600 \text{ mK } a = 3.86276(1) \text{ \AA}$				$c = 12.72035(3) \text{ \AA}$		
Sr	0	0	0.35328(9)	0.27(2)	0.27(2)	0.85(4)
Ru	0	0	0	0.36(3)	0.36(3)	0.01(2)
O(1)	0	0	0.16164(8)	0.13(2)	0.13(2)	0.67(6)
O(2)	0	1/2	0	0.04(1)	0.04(1)	0.30(6)
$R_{wp} = 6.9\%$			$R_e = 6.6\%$			
$T(\text{K}) = 2 \text{ K } a = 3.86276(1) \text{ \AA}$				$c = 12.72038(4) \text{ \AA}$		
Sr	0	0	0.35328(9)	0.60(3)	0.60(3)	0.82(2)
Ru	0	0	0	0.71(3)	0.71(3)	0.92(2)
O(1)	0	0	0.16170(8)	0.10(3)	0.10(3)	0.59(4)
O(2)	0	1/2	0	0.09(6)	0.09(6)	0.21(6)
$R_{wp} = 7.3\%$			$R_e = 8.1\%$			

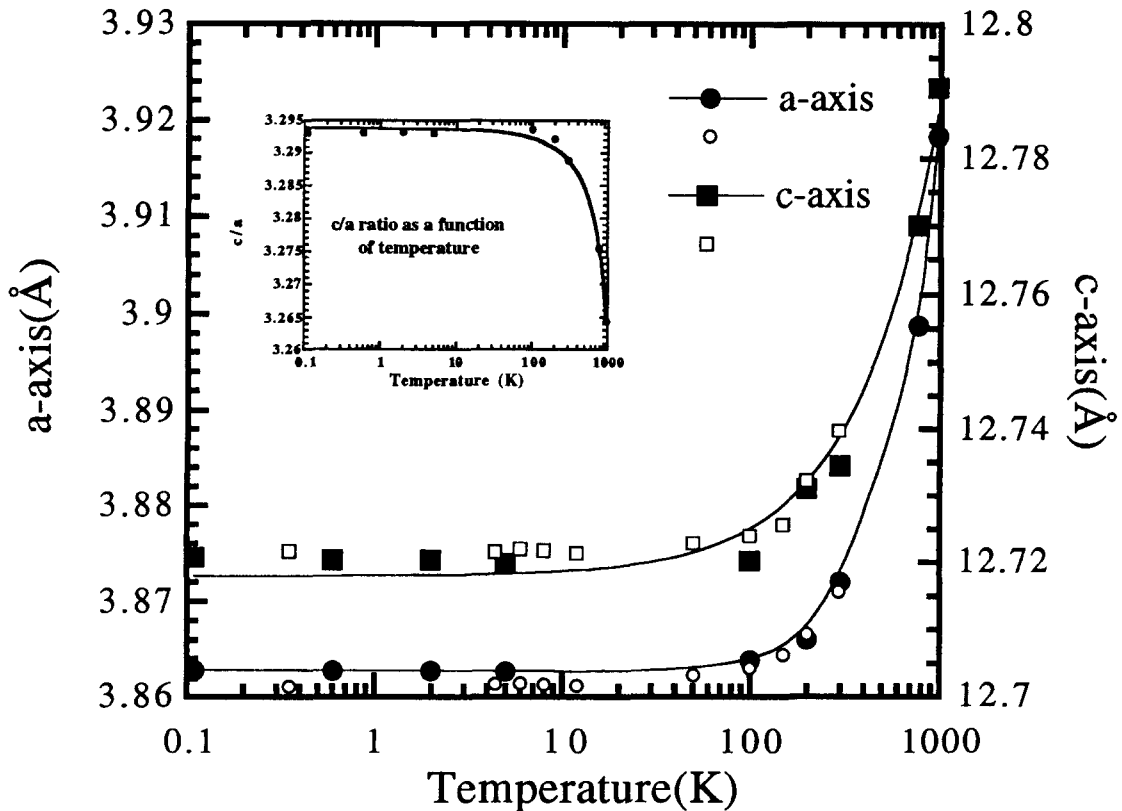


Fig. 4. The variation of the tetragonal lattice parameters of Sr_2RuO_4 as a function of temperature. The solid objects represent the experimental data from this work. Lattice constants from work by Vogt et al. [9] are represented by the open objects. The inset shows the temperature dependence of the ratio of the lattice constants.

the lower curve. No additional peaks, due to long range antiferromagnetic order, were observed at any temperature in this study.

The refined lattice constants of Sr_2RuO_4 and a comparison with the results from Vogt and Buttrey [9] are shown on Fig. 4. The lattice parameters remain constant from base temperature up to 100 K and then they increase steadily up to 973 K. The increase in the lattice parameters above 100 K is a common feature of both these sets of results. Walz and Lichtenberg [10] and Neumeier et al. [6] have reported the refinement of their neutron diffraction data of single crystal and polycrystalline samples of Sr_2RuO_4 between 10 K and 300 K and our parameters agree well with their data at these temperatures. The two different Ru–O distances show a gradual increase with increasing temperature up to 120 K

and then a much sharper increase with temperature above 120 K. Vogt and Buttrey [9] observed a minimum in the temperature dependence of the apical Ru–O distance at 150 K. We have, however, observed no such minimum in our data, but we cannot rule out the possibility of such a minimum from our results because of a lack of data between 100 and 300 K [4]. The ratio of the lattice constants (c/a) is also shown in the inset of Fig. 4. At 120 K a decrease in the ratio of the tetragonal lattice parameters can be seen on warming the sample. This occurs close to the crossover in ρ_c from a non-metallic to metallic state reported by Maeno and coworkers [1] from transport measurements. Haung et al. [11] have also associated this anomaly in the c/a ratio with the crossover from an insulator to a metallic state. Maeno et al. [1] observed no structural

changes in their sample by X-ray measurements and presumed that the change in the ρ_c value at 120 K was purely electronic in origin.

As reported in our previous paper [4], the lattice mismatch between the a -axis of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Y123) and the $a(b)$ -axis of Sr_2RuO_4 was calculated to be 0.12% at 5 K. To the best of our knowledge, low temperature ($T < 1$ K) lattice parameters of $\text{YBa}_2\text{Cu}_3\text{O}_7$ are not available in the literature for comparison, but extrapolating the data from 2 K suggests that the lattice match can only get better.

4. Conclusions

The lattice parameters of the metallic and superconducting strontium ruthenate have been determined by high resolution neutron powder diffraction measurements over a wide temperature range, $110 \text{ mK} < T < 2 \text{ K}$ (this study) and $5 \text{ K} < T < 973 \text{ K}$ (earlier study [4]). We found no evidence for a change in the structure (tetragonal, $I4/mmm$) associated with either the crossover from non-metallic to metallic behaviour at approximately 130 K or at the superconducting transition temperature, 1.15 K. A change in the ratio of the tetragonal lattice constants has been observed at approximately 120 K, this has been associated with the metallic to non-metallic state along the c -axis.

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