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High temperature structural behavior of $SrRuO_3$

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The unusual metal $SrRuO_3$ is perhaps the only known 4*d* transition metal based ferromagnet (T_c = 162K) with a sizable moment. To complement low *T* polarized neutron diffraction measurements of the magnetization density, high *T* neutron diffraction measurements are reported here. Two structural phase transitions are observed. Between 10K and 800K $SrRuO_3$ is orthorhombic and at 800K it appears to be tetragonal until 975K, where it becomes cubic. The temperature variation of the lattice parameters are reported along with a structural description of the tetragonal phase.

Keywords: strontium ruthenate, ferromagnet, perovskite, structural phase transition

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Metallic but nonsuperconducting perovskite oxides, such as $SrRuO_3$, are of interest for thin film device applications incorporating the cuprate superconductors [1]. In addition, the nature of the magnetism and its relationships to the band structure and Fermi-surface properties are of fundamental interest in the context of the widely varied ground states exhibited by the oxide perovskite materials [2]. $SrRuO_3$ is an itinerant ferromagnet with T_c = 162K and 1.2 μ_B/Ru atom. To complement low temperature measurements of the magnetization density in $SrRuO_3$ using polarized neutron diffraction [3], we report here the high temperature crystal structural behavior.

High quality powders were made by reacting Ru metal with $SrCO_3$ at 1273K. Neutron powder diffraction data were collected using the HB4 high resolution powder diffractometer at the High Flux Isotope Reactor, Oak Ridge National Laboratory. Data at 1.5 Å were collected between 10K and 1273K using a closed-cycle He refrigerator for the low temperatures and a vacuum furnace with a Nb heating element for the high temperatures. For the latter, sample temperature was externally calibrated using the thermal expansion of MgO. Selected portions of the diffraction pattern were also surveyed between 296K and 1173K using 1.1166 Å x-rays at the NSLS.

No structural phase transitions occur between 10K and 800K; the structure remains orthorhombic [4], *Pnma*, but the orthorhombicity, decreases markedly above room temperature (Fig. 1a). At 800K $SrRuO_3$ appears to be metrically tetragonal until 975K, where it becomes cubic. In the tetragonal region the space group *I4/mcm* provides a good fit to the neutron data and is consistent with the synchrotron data. Structural parameters representative of each of the three phase fields are given in Table 1. The *Pnma* structure is an example of a three-tilt system, where the octahedra remain rigid, and the *I4/mcm* structure is a single-tilt system [5]. This implies that the change from one to the other is discontinuous,

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in the sense that a smooth undoing of the octahedral rotations does not occur; otherwise, intermediate structures with different space group symmetries would be expected. For our measurement resolution, other structural symmetries, either above or below the orthorhombic ↔ tetragonal transition, could not be confirmed. Nevertheless, the phase transformations are displacive in nature, i.e., no bond breaking. Other studies of $SrRuO_3$ also have observed indications of a similar series of phase transitions with increasing T [6]. The cell volume expansion fit above T_c using a Debye model gives $V_0 = 241.22(5)$ Å^3, $\theta_D = 601(41)$K, and $9\gamma NK_B/B = 0.0273(3)$ Å^3/K (Fig. 1b). Kiyama et al. show by comparison with $CaRuO_3$, that for $SrRuO_3$ the lattice contraction below T_c is anomalous due to the magnetovolume effect [7]. Least-squares analysis of the temperature dependence of the lattice parameters for the orthorhombic portion (10K to 800K) gives the following $a = 5.5311 - 8.173 \times 10^{-6}T + 8.539 \times 10^{-8}T^2$ Å, $b = 7.8424 + 1.282 \times 10^{-6}T + 1.019 \times 10^{-7}T^2 - 4.357 \times 10^{-11}T^3$ Å, $c = 5.5631 + 2.146 \times 10^{-5}T + 3.552 \times 10^{-8}\ T^2$ Å, where T is in K. The volume fit over the entire T interval (10K to 1275K) is $V = 241.35 - 5.918 \times 10^{-5}T + 1.129 \times 10^{-5}T^2 - 4.224 \times 10^{-9}T^3$ Å^3

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Table 1. Crystal Structure Data for $SrRuO_3$.

300K,
Pnma, a=5.5368(2)Å, b=7.8523(3)Å, c=5.5731(2)Å

atom	x	y	z	U_{iso} (Å^2)
Sr	0.0162(6)	1/4	-0.0016(7)	0.0100(4)
Ru	1/2	0	0	0.0072(3)
O1	-0.0034(7)	1/4	0.4492(7)	0.0102(7)
O2	0.2232(4)	-0.0270(3)	0.2235(4)	0.0114(6)

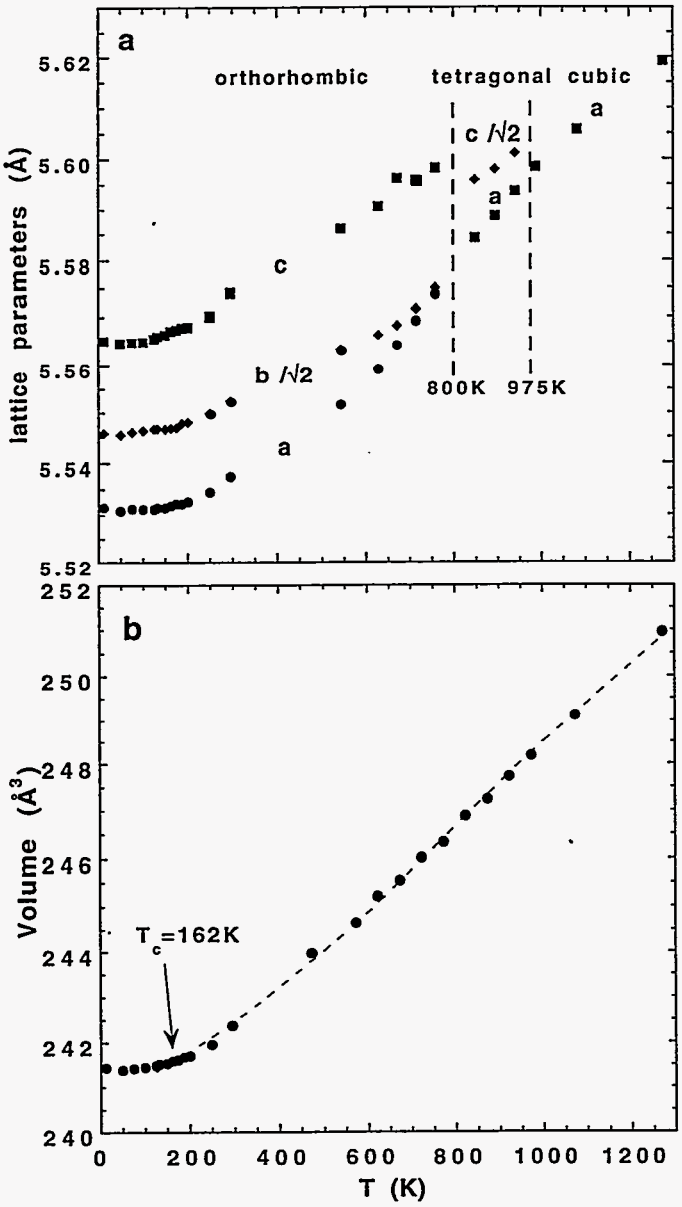
894K, *I4/mcm*, a=5.5887(1)Å, c=7.9168(4)Å

atom	x	y	z	U_{iso} (Å^2)
Sr	0	1/2	1/4	0.0237(5)
Ru	0	0	0	0.0097(4)
O1	0	0	1/4	0.026(2)
O2	0.2275(4)	0.7275	0	0.032(1)

1082K, *Pm* $\bar{3}m$, a=3.9735(1)Å

atom	x	y	z	U_{iso} (Å^2)
Sr	1/2	1/2	1/2	0.0309(4)
Ru	0	0	0	0.0138(3)
O	1/2	0	0	0.0424(4)

Fig. 1. a. $SrRuO_3$ lattice parameters as a function of T. b. Cell volume versus T, where the fitted line is for a Debye model (see text and reference [7] for details).


a
orthorhombic
tetragonal
cubic
c /√2
a
c
b /√2
a
800K
975K
lattice parameters (Å)
5.62
5.60
5.58
5.56
5.54
5.52
b
Volume (Å³)
252
250
248
246
244
242
240
T_c=162K
0
200
400
600
800
1000
1200
T (K)