

THERMODYNAMICS OF THE La-Sr-Cu-O HIGH T<sub>c</sub> SUPERCONDUCTORS:  
HEAT CAPACITIES OF SrCuO<sub>2</sub>, Sr<sub>2</sub>CuO<sub>3</sub>, Sr<sub>14</sub>Cu<sub>24</sub>O<sub>41</sub>,  
and (La<sub>1-x</sub>Sr<sub>x</sub>)CuO<sub>4-x</sub> (x = 0.00, 0.05, 0.30, 0.5)

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ABSTRACT

The subambient heat capacities of seven La-Sr-Cu-O samples were measured by adiabatic calorimetry over the temperature range 5 to 350 K. The heat capacity of Sr<sub>14</sub>Cu<sub>24</sub>O<sub>41</sub> was derived from that of the mixed phase of nominal composition SrO:CuO = 1:2. No anomalous contribution was identified in the heat capacities of SrCuO<sub>2</sub>, Sr<sub>2</sub>CuO<sub>3</sub>, Sr<sub>14</sub>Cu<sub>24</sub>O<sub>41</sub>, LaSrCuO<sub>3.5</sub> and La<sub>2</sub>CuO<sub>3</sub>. A small anomaly associated with the orthorhombic to tetragonal transformation was identified at the vicinity of 300 K in the heat capacity of La<sub>1.90</sub>Sr<sub>0.10</sub>CuO<sub>3.90</sub>. Onset of Meisner effects in the magnetic susceptibilities of La<sub>1.90</sub>Sr<sub>0.10</sub>CuO<sub>3.90</sub> and La<sub>1.4</sub>Sr<sub>0.6</sub>CuO<sub>3.7</sub> were identified at about 32 and 36 K respectively. The onset of superconductivity in these samples is not accompanied by a break in the heat capacity at the critical temperatures. A series of thermal history dependent anomalies were identified in the heat capacity, magnetic susceptibility and electrical conductivity of La<sub>1.4</sub>Sr<sub>0.6</sub>CuO<sub>3.7</sub> between 234 and 290 K. Annealing at 234 K causes the anomalies to shift to higher temperatures. Cooling below the transition temperature restores the anomalies. The anomalies tend to disappear after prolonged annealing at 380 K in air.

INTRODUCTION

The La-Sr-Cu-O (LSCO) chemical system which shows an unusual array of electric and magnetic properties is in the focus of much scientific activity since the discovery of superconductivity above 30 K in this, and in other chemically related, systems. The thermodynamic properties of this system have been the center of a broad investigation in which the subambient heat capacities, superambient electrochemical properties, magnetic susceptibilities, and electrical resistivities of seven samples have been studied. This thorough investigation has been the subject of several recent communications.<sup>1-5</sup> The samples used in the studies and their compositions are listed in Table I. For clear identification and easier communication the compounds studied are designated with Roman numerals I - VII. This designation is especially useful when the composition of the sample used in the experiment is different than that of a stable phase. This is the case with the sample whose nominal composition is SrCu<sub>2</sub>O<sub>3+x</sub> which is believed to consist of the two stable compounds CuO and Sr<sub>14</sub>Cu<sub>24</sub>O<sub>41</sub>. All the other samples are believed to be of stable single-phase compositions.

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Table I Compounds and designations in this study

Formula	Designation	M/g•mol <sup>-1</sup>	Ref.
SrCuO <sub>2</sub> ,	I	183.166	1
Sr <sub>2</sub> CuO <sub>3</sub> ,	II	286.785	1
Sr <sub>14</sub> Cu <sub>24</sub> O <sub>41</sub> ,	III	3407.764	1
La <sub>1.9</sub> Sr <sub>0.1</sub> CuO <sub>3.95</sub>	IV	399.437	2
La <sub>1.4</sub> Sr <sub>0.6</sub> CuO <sub>3.70</sub>	V	369.792	2
LaSrCuO <sub>3.50</sub>	VI	346.076	3
La <sub>2</sub> CuO <sub>4</sub>	VII	405.366	3

This report makes no attempt to repeat the material that we have already published, submitted, or committed to other channels of communications. The major goal of the authors here is to supplement their previous communications and to attempt to summarize and unify our research efforts concerning this chemical system under one title. The readers are referred to references 1 through 5 for further details regarding experimental procedures, sample preparation, tabulated data, thermophysical properties, and further discussion.

### EXPERIMENTAL

The oxide samples were prepared by a conventional ceramic mixing technique using high purity SrCO<sub>3</sub>, CuO, and La<sub>2</sub>O<sub>3</sub>. All samples were pressed into pellets (under a pressure of 10,000 Kg•Cm<sup>-2</sup>) and sintered in air. X-ray analysis was used to confirm the existence of a single-phase product. The sample whose Sr/Cu composition ratio was 1/2 was found to consist of at least two phases of which one is the oxygen rich phase Sr<sub>14</sub>Cu<sub>24</sub>O<sub>41</sub> and the other is excess CuO. Chemical analysis of this sample revealed the presence of carbonate ion (about 0.03 % by mass of carbon).

The subambient heat capacities of the seven samples were measured in an adiabatic calorimetric cryostat (laboratory designated Mark XIII<sup>6, 7</sup>) from 5.3 to 350 K. The same gold plated, oxygen-free, high-conductivity, (OFHC) copper calorimeter (laboratory designation W-99) was used for all samples. Samples massing between 20 and 35 g were used in these experiments.

The magnetic susceptibilities at 50 Gauss of about 1 g samples of La<sub>1.9</sub>Sr<sub>0.1</sub>CuO<sub>3.95</sub> (between 4 and 60 K) and La<sub>1.4</sub>Sr<sub>0.6</sub>CuO<sub>3.70</sub> (between 2 and 300 K) and the electrical resistivity of the former (between 2.4 and 333 K) were measured using a SQUID magnetometer (Quantum Design). Powder samples were used for the susceptibility measurements and two different pelleted (of different thermal history) samples were used for the measurements of electrical resistivity.

### RESULTS AND DISCUSSION

#### SrCuO<sub>2</sub>, Sr<sub>2</sub>CuO<sub>3</sub>, and Sr<sub>14</sub>Cu<sub>24</sub>O<sub>41</sub>

As indicated above the tabulated experimental results and their graphical representations are presented elsewhere.<sup>1-3</sup> The first three compounds in the series

(I-III) show no anomalous contribution apart from the lattice and electronic heat capacities. While the thermodynamic properties of I can be well approximated as a sum of the properties of CuO and SrO this is not the case for compounds II and III. All three compounds exhibit Debye-like behavior at low temperatures with a small but finite Sommerfeld coefficient.

The actual stoichiometry of the third sample was  $\text{Sr}_{14}\text{Cu}_{28}\text{O}_{45}$  and it is believed to contain two phases,  $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$  and CuO. The mass ratio between the phases was calculated as 91.54/8.46. The existence of the oxygen rich compound  $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$  was reported by several authors<sup>8,9</sup> and was supported by thermogravimetric analysis of our sample. However, more recently it was suggested that the apparent excess oxygen in the sample may be due to a small residue of carbonate ions which remain in the sample after synthesis.<sup>10</sup> Consequently our sample was analyzed for any excess carbonate and small traces of carbonate ions (0.178 % carbon by mass) were identified. It is not yet clear whether this amount of carbonate ions can explain the oxygen stoichiometry and the physical properties of the sample. It should be noted in this context that the magnetic transition characteristic of CuO between 210 and 240 K cannot be found in the heat capacity of this sample although well within the precision of the experiments. The absence of these transitions may suggest that the sample is more complex than a simple mixture of  $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$  and CuO.

$\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_{3.95}$  and  $\text{La}_{1.4}\text{Sr}_{0.6}\text{CuO}_{3.70}$

Compounds IV and V are high  $T_c$  superconductors with critical temperatures of 32 and 36 K respectively. However, no break in the heat capacity curve of either compound is observed at the critical temperature for superconductivity. Heat capacity breaks in the heat capacity of IV ( $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_{3.95}$ ) or samples of very close composition were observed by several authors.<sup>11</sup> However, the existence and magnitude of the break depends on the uniformity of the sample, sample preparation methods, and exact stoichiometry. There is not yet an agreement in the literature concerning the magnitude of the break and its dependence on stoichiometry in this chemical system. In contrast to classical superconductors, the transformation from normal state to the superconducting state in this system is broad, as evident from the magnetic susceptibilities of these samples.<sup>2</sup> This broadness may mask the break in the heat capacity. It is also evident that the transformation to the superconducting state in V is not complete and even at 4 K only about 1 % of the material is superconducting. The magnitude of the Meissner effect in IV is about an order of magnitude larger than that of V under the same conditions. During the course of the heat-capacity measurement two series of runs through the critical temperature region of IV were conducted. Three series of measurement through the critical temperature region were conducted for sample V.

A small hump in the heat capacity of IV was observed at about 300 K. This excess contribution is associated with the orthorhombic to tetragonal transformation at that temperature. The agreement of this transition temperature with literature values strongly supports the sample composition reported here and provides further evidence for its being a single phase.

### Anomalies Between 230 and 290 K

Anomalous behavior is observed in the heat capacity, magnetic susceptibility, and electrical resistivity of  $\text{V}(\text{La}_{1.4}\text{Sr}_{0.6}\text{CuO}_{3.70})$  between 234 and 290 K.<sup>2</sup> These anomalies are strongly dependent on the thermal history of the sample. Annealing the sample at or slightly above the temperatures in which an anomaly is observed tends to suppress the phenomena. Consequently, repeating a measurement does not necessarily reproduce the same results since the thermal history of the specimen was affected by the previous measurement. However, measurements taken under the same condition and the same thermal history tend to be reproducible.

During the course of the heat-capacity experiment, three series of measurements were conducted. Prior to the first series the sample (which was quenched from 1050 K to room temperature during synthesis and was maintained at that temperature) was cooled to 4.9 K and was heated slowly during the course of the measurement. The sample was heated and cooled through the critical temperature (36 K) three times during that experiment before being heated through the region in which the anomalous contributions were observed. Three peaks, each larger than the experimental uncertainty at that temperature, are observed in the heat-capacity curve between 234 and 290 K. These anomalies were not reproduced in the next two series of heat-capacity measurements. The sample was cooled slowly to 180 K and to 190 K, respectively, prior to these two series of measurements. No anomalous behavior was observed in either series.

Two sets of susceptibility measurements over the temperature region 200 to 300 K were conducted using a 1 g powdered sample. For the first set the sample was cooled from 303 to 200 K during the course of the measurement. For the second set the sample was cooled to liquid helium temperature, maintained at that temperature for some time then heated to 200 K and the measurement repeated. The two sets of measurements clearly disagree although performed on the same sample, (which was not removed from the magnetometer) during experiments on a given sample.

An approximate 1 g portion of the sample used for the heat capacity measurement was pelleted and sintered at 1050 K for about 48 hours. The pellet was then quenched to room temperature and cut into several rods. The electrical resistivity of two of these rods was measured between 2.4 and 330 K. At low temperatures the sample is a semiconductor with a small decrease in the resistivity at the critical temperature for superconductivity (ref. 2 figure 6). The resistivity between the critical temperature and 234 K is almost constant. At 234 K an increase of two orders of magnitude in the resistivity is observed for the first sample rod. The magnitude of the jump varies with thermal history and heating rate. Maintaining the sample at 234 K causes the resistivity at that temperature to return to its pre 234 K level and the anomaly is shifted to a higher temperature. The same phenomena reoccurs upon annealing the sample at the temperature to which the anomaly is shifted. However, the annealing time required to suppress the anomaly increases with temperature. The anomaly is restored only upon cooling below the critical temperature, although the exact temperature to which the sample has to be cooled was not identified. Both the resistivity anomaly and its dependence on thermal history are reproducible. The second sample rod was annealed at 380 K in air prior to the resistivity measurement. No anomalous behavior is observed in the resistivity of this sample. It is believed that the different thermal history of these samples accounts for the difference in properties.

Anomalous behavior of thermophysical properties of high  $T_c$  superconductors, between 200 and 300 K, have been previously reported.<sup>11</sup> However these

anomalies tend to be irreproducible and were often described as the "now you see it now you don't" phenomena. The anomalies reported here do not fit the above terminology; they are all reproducible and their dependence on thermal history is characterized. The dependence of these anomalies on thermal history and their tendency to shift to higher temperatures upon annealing explains the oddly shaped heat-capacity curve between 230 and 290 K. It is likely that these series of anomalies observed over that temperature region are a single anomaly which is propagating to higher temperature as the sample temperature increases. Various methods of heat-capacity measurements (such as scanning calorimetry, AC, or continuous heating methods) may reveal a variety of apparently different anomalies as a function of heating rates and thermal histories.

#### LaSrCuO<sub>3.50</sub> and La<sub>2</sub>CuO<sub>4</sub>

The major motivation for measuring the heat capacities of these two compounds<sup>3</sup> is to assist in the development of an interpolation method between compounds of different stoichiometry within the same chemical system. Substitution of La in La<sub>2</sub>CuO<sub>4</sub> with Sr allows for the compositions which produce high  $T_c$  superconductivity. Thus by simple chemical substitution one may move almost freely from La<sub>2</sub>CuO<sub>4</sub> (VII) through LaSrCuO<sub>3.50</sub> (VI) to Sr<sub>2</sub>CuO<sub>3</sub> (II). Thus knowing the thermophysical properties of these three phases, an interpolation method may be developed and the properties of related compounds may then be calculated. A similar interpolation method has been previously developed by the authors for other chemical systems such as the lanthanide sesquisulfides.<sup>6,12</sup> These methods take advantage of developments in macroscopic properties such as the molar volumes,<sup>13</sup> masses, or combinations of the two.<sup>14</sup> Once such a method is obtained a "generic" heat capacity for compounds in this chemical system may be generated and the lattice contribution to the heat capacity of compounds of any given composition within the system may readily be calculated. The development of such an interpolation system along with the analysis of the heat capacities of VI and VII are the subject of reference 3.

#### ACKNOWLEDGMENTS

The authors wish to acknowledge John Shewchun for his assistance in the magnetic susceptibility and electrical resistivity measurements. The preparation of this manuscript at the University of Illinois at Chicago was supported by the Solid State Chemistry Program of the Division of Materials Research of the National Science Foundation under grant DMR-8815798.

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