

DOE/ER/45630--1
DE-FG02-97ER45630--1

**Properties of Doped Bi-Based Superconductors
South Carolina State University**

**Final Technical Report For The Contract Period
June 1, 1997 to May 31, 2001**

**James E. Payne
Department of Physical Sciences
South Carolina State University
Orangeburg, SC**

August, 2001

DOE Patent Clearance Granted
MPDvorscak
Mark P. Dvorscak
(630) 252-2393
E-mail: mark.dvorscak@ch.doe.gov
Office of Intellectual Property Law
DOE Chicago Operations Office
9/24/2002
Date

**Prepared for the U. S. Department of Energy
Under Contract DE-FG0297ER45630**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

INTRODUCTION

Proposal Justification

This initiative was the result of a previous collaborative effort of South Carolina State University a land grant, historically black university and Clemson University, a land grant institution having South Carolina's largest science and technology programs. One of the goals of this initial effort was to posture South Carolina State University to submit meritorious proposals

South Carolina State University (SCSU) has a total undergraduate and graduate enrollment of approximately five thousand, of whom over ninety percent are members of ethnic minority groups. There is strong emphasis on undergraduate education in the physical sciences and a desire to extend into a graduate program. In the Department of Physical Sciences there has been faculty involvement in DOE-supported research through the Savannah River Technical Center (SRTC). SCSU has had research ties with other universities, Clemson University (CU) and the University of South Carolina (USC) in particular, both through direct interactions and through the DOE-supported South Carolina University Research and Education Foundation (SCUREF). The collaboration between SCSU and CU has continued as a component of this work.

Research Problem Selection

The selection of a research problem was based primarily on two factors:

1. There was inadequate single-crystal specific heat and thermal conductivity data for the cuprate high temperature superconductors, particularly the BiSCCO compounds with the general formula $\text{Bi}_x\text{Sr}_{1-x}\text{Ca}_{n-1}\text{Cu}_n\text{O}_p$, where $n=1,2,3$. These two thermophysical properties as determined on well-characterized samples, give direct insight into the origin of cuprate superconductivity and the microscopic nature of the superconducting state. Moreover, an improved knowledge of these properties is needed for the processing and application of useful superconducting components.

2. As a result of the previous work there exists at both universities extensive expertise and experience in the growth, manipulation and study of the properties of microcrystals ("whiskers") of various materials. Furthermore, there is prior experience in calorimetry in both faculty groups. It was known that whiskers of the Bi-based cuprates could be grown from a precursor of quenched glass shards and that this is influenced by the addition of doping materials.

A research plan was prepared for measuring the specific heat and thermal conductivity of BiSCCO microcrystals, taking advantage of the combined capabilities and resources of SCSU and CU. A primary focus would be the measurement of the thermophysical properties of the doped samples.

An essential component of the work would involve the careful and complete characterization of the microcrystal samples on which the measurements would be made. Also available would be the results of the previous work on these materials.

Early emphasis would be given to measurements at temperatures in the neighborhood of the superconducting transition, delineating electron and phonon anomalies and contributing to an understanding of the nature of the transition. The literature indicated that the specific heat anomaly in the BiSCCO's was small. This fact, together with the

expectation that the microcrystal samples would probably have masses in the microgram range, indicated that considerable effort would be required initially to select and develop the experimental approach for the calorimetry and for the thermal conductivity measurements.

It was planned that a CU graduate student would do his or her thesis research at SCSU and that SCSU undergraduates would also be involved in the research.

A wide range of characterization tools would be needed, especially adapted to microgram-mass crystals, so that measurements could be made on well-defined and characterized materials. The expected needs included:

- * R vs. T
- * Thermopower
- * Magnetic Flux Shielding
- * X-Ray and Electron Diffraction
- * Electron and Optical Metallography
- * Microprobe and Wet Chemical Analysis.

All of these characterization tools were not expected to be available at SCSU and CU, so the involvement of external collaborators was anticipated.

A proposal based on this plan and describing expected accomplishments during a three-year grant period was submitted to the Division of Materials Sciences, Office of Basic Energy Sciences, U. S. Department of Energy in May, 1992.

A year-by-year summary of accomplishments is provided below. A list of publications and presentations at scientific meetings follows the summary. Appendix I contains copies of papers both submitted and in print as a result of this project.

NOTEWORTHY ACCOMPLISHMENTS

- 16 Undergraduates have participated in the research
 - All undergraduates have given presentations at regional or national meeting
- An African American graduate student was supported and will receive his Ph.D. in December of 2001
- The development of the research capabilities at SCSU has led to funded research from NASA and NSF

RESEARCH ACCOMPLISHMENTS

Contract Period-June 1, 1997 to December 31, 1998.

Research Progress:

The sample production is progressing with the production of highly doped single crystal samples and bulk samples.

a) Single crystals of BiSCCO materials doped with Fe are being studied. It had been observed that the starting compound used for iron doping affects the transition temperature. The effect is being examined with both resistance measurements and thermal conductivity measurements.

b) In attempts to study the effects of high levels of gold and silver doping, samples are being prepared using pellets of the BiSCCO materials with doping levels as high as 20%. These samples will be studied using resistance versus temperature measurements and a SQUID magnetometer.

Collaboration with Clemson University:

As outlined in the proposal, the collaboration with Clemson University is being continued. The personnel at South Carolina State University (SCSU) and the personnel from Clemson

University (CU) have made visits to each site on a regular basis to maintain continuity in the program. In addition, the SCSU personnel have consulted the personnel at Clemson concerning the selection of the person for the post-doctoral position.

Other Collaborations

The availability of the thermal conductivity apparatus has led to additional collaborations with researchers studying new materials for thermoelectric coolers. This group is led by Dr. Terry Tritt of Clemson University.

Contract Period -January 1, 1999 to May 31, 2001.

Research Progress:

Sample Preparation

Two approaches have been undertaken in the preparation of samples for analysis. Bulk samples have been produced by pressing the materials into pellets. These samples contain various amounts of silver (Ag) or gold (Au) being substituted for the copper in the materials. Substitution levels for silver range from 0.5% to 20%. As a parallel to this process samples of "glass" have been prepared by a melt quench process for the growth of single crystals (whiskers) with the same substitution levels of silver. The process and the levels of uptake of substituted material have been reported by one of the undergraduates at a national meeting.

Sample Analysis

The samples are analyzed using an electron microscope equipped with a microprobe and by measuring the resistance of the sample as a function of temperature. From the microprobe data it is possible to determine the amount of substituted material that is incorporated into the whiskers. The microprobe is also used to examine the distribution of substituted material in the pellets. Since both silver and gold are in the same column of the periodic table as copper it was expected that this substitution would affect the transition temperature of the superconductors in some regular fashion.

Results to Date

In figure 1, a typical transition curve for a substituted pellets shows the presence of both the 2223 phase (transition temperature of approximately 105K) and the 2212 phase (transition temperature of approximately 70K). Data for the whiskers indicates that the 2223 phase is the major contributor but from other analysis it can be shown that only a small fraction of the whisker is 2223 but this small amount appears to "short" the other phase. The microprobe results for the silver incorporated in a whisker indicate that the level of silver is not above background. The distribution of silver within a pellet is very uniform, but this is not an indication of the material being incorporated into the superconducting phases. Figure 3 is a plot of transition temperature as a function of dopant level, x , for silver in the material. There is no consistent effect and any variation is within error. The indications are that silver is not incorporated into the whiskers or the superconducting phase within the pellets.

Collaboration with Clemson University:

As outlined in the proposal, the collaboration with Clemson University is being continued. The personnel at South Carolina State University (SCSU) and the personnel from Clemson University (CU) have made visits to each site on a regular basis to maintain continuity in the program. In addition, the SCSU personnel have consulted the personnel at Clemson concerning the selection of the person for the post-doctoral position. A graduate student, Mr. Bryan Gamble, is beginning his doctoral research at Clemson and will carry out part of his work at SCSU.

Other Collaborations

The availability of the thermal conductivity apparatus has led to additional collaborations with researchers studying new materials for thermoelectric coolers. This group is led by Dr. Terry Tritt of Clemson University.

PERSONNEL

Contract Period-June 1, 1997 to December 31, 1998.

Faculty

Dr. James E. Payne has devoted 50% of his time to the project during the summer.

Dr. Darren Verebelyi worked on the project until October as a post-doctoral researcher.

Undergraduate Students

One undergraduate student, Mr. Jamie Henderson, was employed during the summer but was unable to continue during the academic year due to other scholarship commitments.

Three students, Mr. Marcus Pepper, Ms. Francis Epps and Ms. Kelry Robinson are currently working as research assistants on the program.

Post-Doctoral Researcher

Efforts have been underway since July to secure a Post-doc. Several very promising candidates have been identified and an offer will be made during second semester.

Summer Mentor Student

A rising high school senior was involved with the research during the summer as part of the South Carolina Governor's School for Science and Math Summer Mentor Program. The student was supported by the Mentor Program and studied the effects of elevated temperature on the phases in the single crystals.

Contract Period -January 1, 1999 to May 31, 2001.

Faculty

Dr. James E. Payne has devoted 50% of his time to the project during the summer.

Dr. Payne devoted 25% of his time during the academic year to the project.

Undergraduate Students

Two undergraduate students, Ms. Kelry Robinson and Mr. Lyjohn Fride, were employed during the summer and were able to continue during the first semester of the academic year. Ms. Robinson is a candidate for graduation in December but Mr. Fride will continue on the project.

Mr. Marcus Pepper was employed for the academic year.

Post-Doctoral Researcher

Dr. Jonathan Obien has accepted a position as post-doctoral researcher on the project and will start no later than January 15, 1999. It has been necessary to delay the start date due to his other commitments and arrangements for a visa.

Summer Mentor Student

A rising high school senior will be selected during the spring for a position with the research project during the summer as part of the South Carolina Governor's School for Science and Mathematics Summer Mentor Program.

Minority Student Participation During Contract Period

As noted in the foregoing narrative, there was extensive involvement of undergraduate students in the research at SCSU. A list of the students follows, with a parenthetical notation of those students who entered graduate school on completion of their undergraduate studies:

Bruce Haywood (grad school physic)
Chris Dixon (grad school physics)
Jermaine Hampton (grad school physics)
Francis Epps (senior SCSU)
Bobby Epps (grad school environmental science)
David Irick (navy research)
Jamie Henderson (grad school)
Michael Gaillard (grad intern ORNL)
Ronald Wilson
Marcus Pepper
Phillip Campbell (grad school)
Bernard Jackson (grad school)
Erica Lamar (senior SCSU)
Michael Collingwood (senior SCSU)
Lyjohn Fride (grad school physics)
Durwayn Duncan (junior SCSU)

Most of these students were involved in oral presentations of their work at the following meetings and conferences:

Five presentations at the South Carolina Academy of Sciences;

Three presentations at the annual meeting of the South Carolina Alliance for Minority Participation (SCAMP);

Two presentations at the National Meeting of the Alliance for Minority Participation;

Two presentations at the National Meeting of Black Physics Students;

Five presentations at the Conference of the South Carolina Governors School for Science and Mathematics Student Research.

DISSERTATIONS

"Heat Capacity and Transport properties of Diantimonides"
Bryan Gamble

PUBLICATIONS AND ORAL PRESENTATIONS

M. Chung, D. T. Verebelyi, C. W. Schneider, M. V. Nevitt, M. J. Skove, J. E. Payne, M. Marone and P. Kostic', "Characterization of Bi Based Superconducting Whiskers", Physica B (in press).

D. T. Verebelyi, "Thermal Conductivity Measurements of Microgram Superconducting Bi-Sr-Ca-Cu-O (2212) Whiskers", Review of Scientific Instruments, March, 1997

Y. K. Kuo, C. W. Schneider, M. J. Skove, M. V. Nevitt, G. X. Tessema and J. J. McGee, "Effect of Magnetic and Nonmagnetic Impurities (Ni, Zn) substitutions for Cu in $\text{Bi}_2(\text{SrCa})_{2+n}[(\text{Cu}_{1-x}\text{M}_x)_{(1+n)}\text{O}_y]$ Whiskers," Phys. Rev. B56 (1997) 6201.

Y. K. Kuo, M. J. Skove, D. T. Verebelyi, H. Li, R. MacKay, S. -J. Hwu, M. -H. Wangbo and J. W. Brill, "Unusual Physical Properties of $\text{KCu}_{(7-x)}\text{S}_4$ at Diffusive One-Dimensional Ordering Transitions," Phys. Rev. B57 (1998) 3315.

Y. K. Kuo, C. W. Schneider, M. V. Nevitt, J. J. Skove and G. X. Tessema, "The Effect of Co Substitution for Cu in $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{9(8-d)}$ " Phys. Rev. B (in press)

Y. K. Kuo and C. V. Schneider, "Substitution of Transition Metals for Cu in $\text{Bi}_2(\text{Sr, Ca})_{n+1}[\text{Cu}_{x-1}\text{M}_x]_n\text{O}_{6+2n}$ Single Crystal Whiskers," (in prep).

Appendix I
Figures 1,2, and 3

Transition Curve for a Whisker

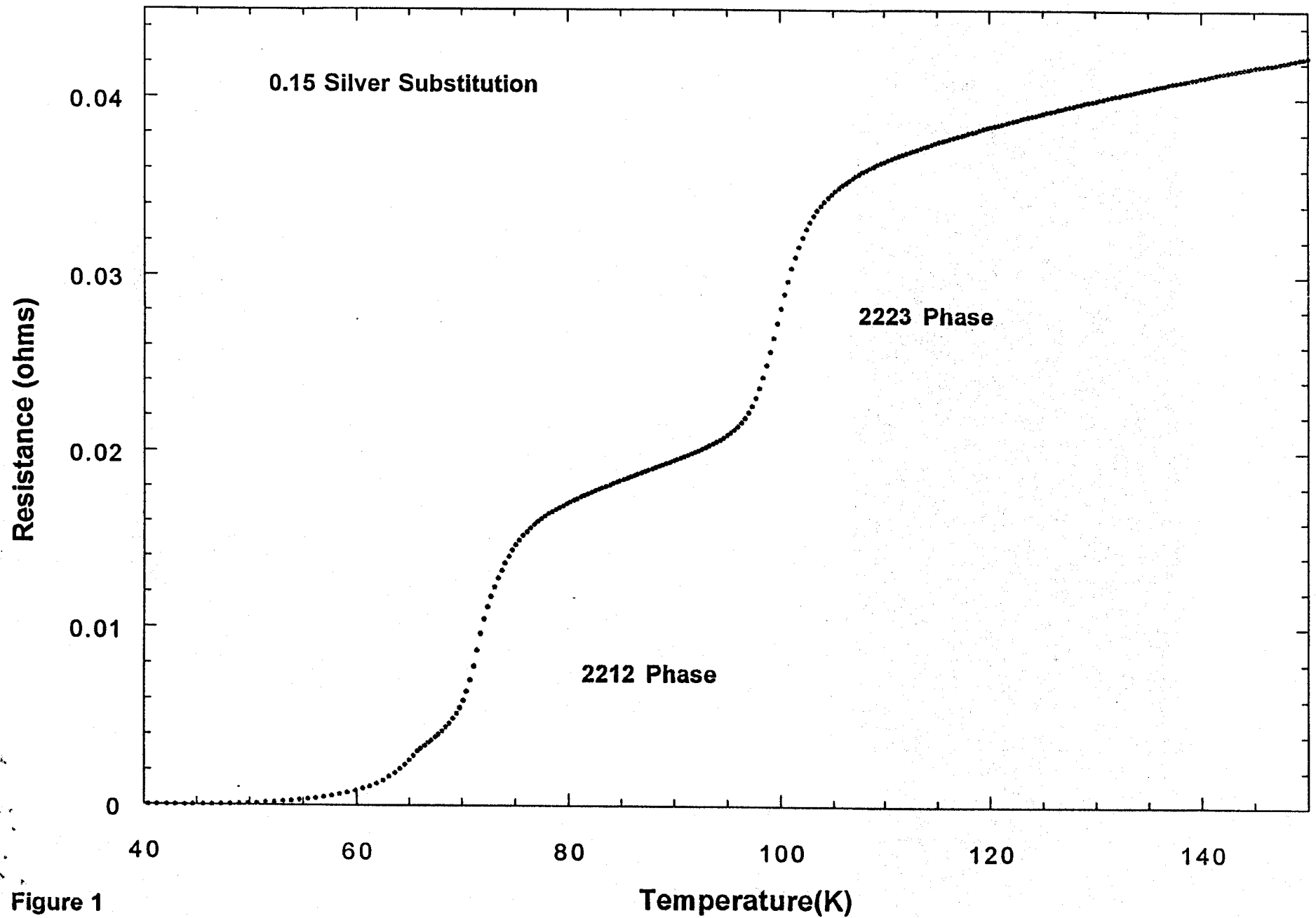


Figure 1

Normalized Resistance for Silver Doped Pellets

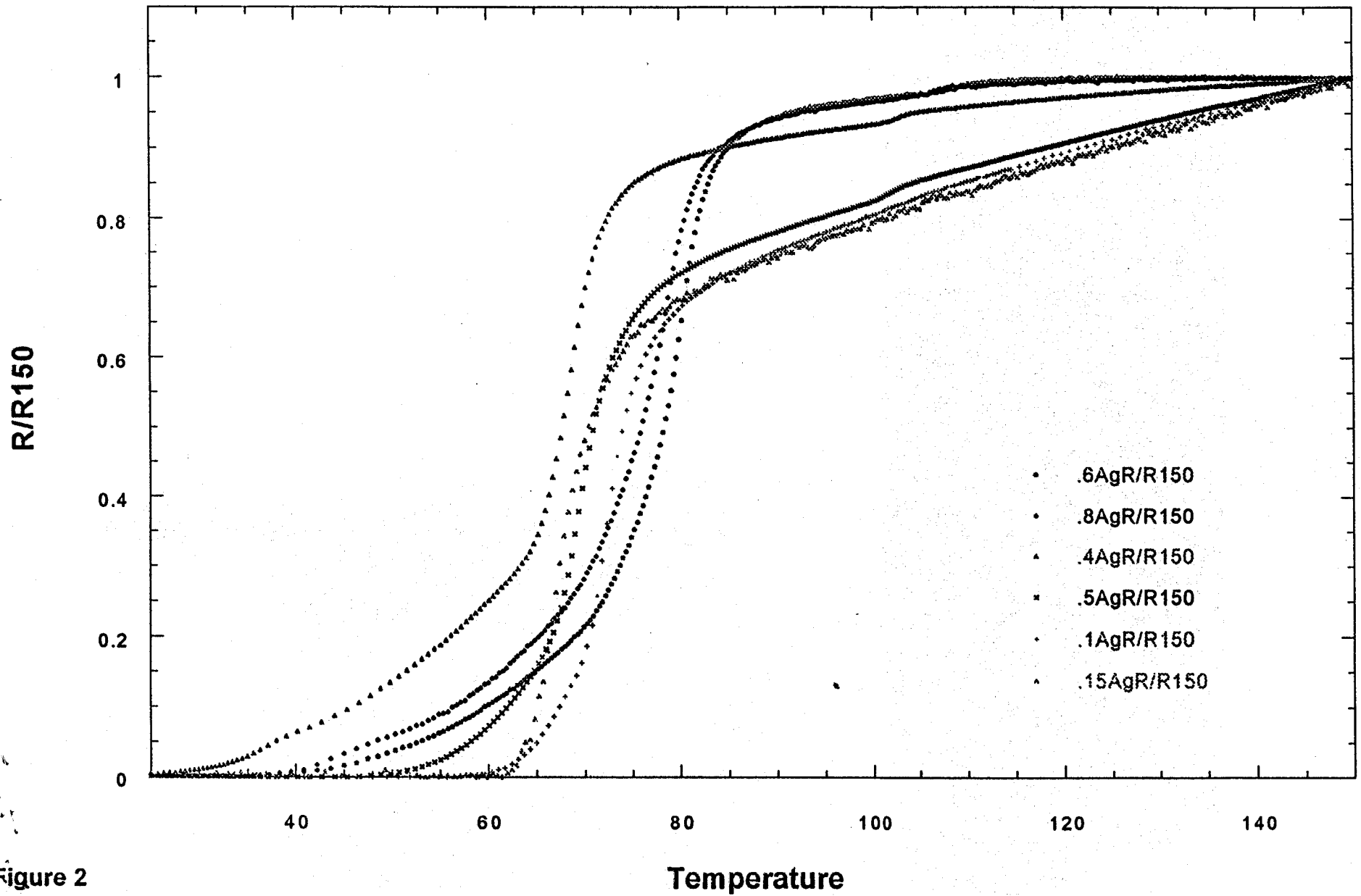


Figure 2

Effect of Substitution on T_c

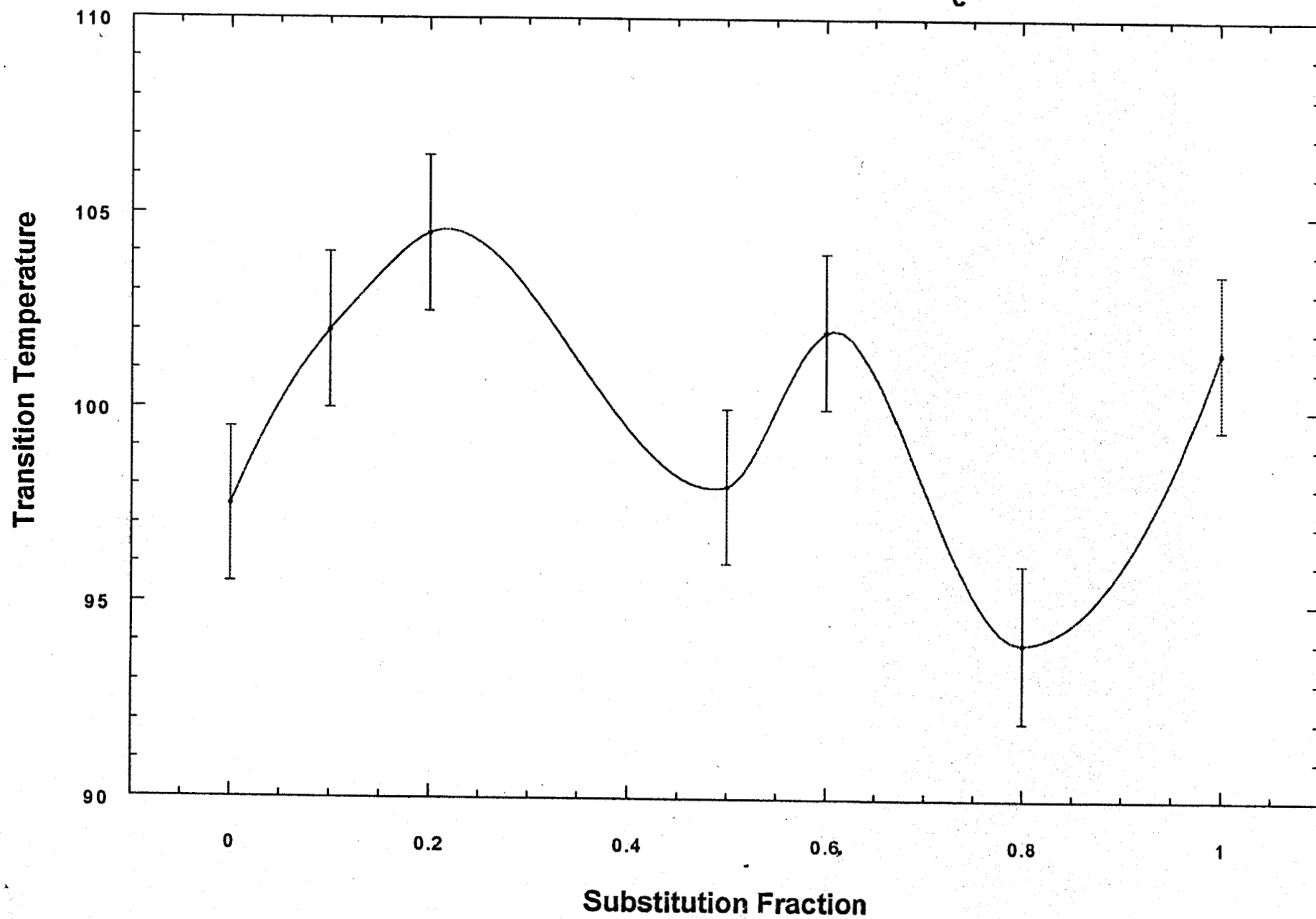


figure 3