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Author(s):

Albert Migliori, MST-10
 Paul Canfield, Iowa State University, Ames
 W. Clark, UCLA
 Zachary Fisk, MST
 Ming Lei, MST-10
 David Mandrus, P-10
 John Sarrao, P-10
 Joe Thompson, MST-10
 Stuart Trugman, T-11

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Structural Phase Transitions in Non-Stoichiometric Oxides and Other Materials

Albert Migliori*, Paul Canfield (Iowa State University, Ames), W. Clark (UCLA),
Zachary Fisk, Ming Lei, David Mandrus, John Sarrao,
Joe Thompson, and Stuart Trugman

Abstract

This is the final report of a three-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). Structural phase transitions (SPT) have profound effects on mechanical, magnetic, and electronic properties. In some stoichiometric compounds, SPTs are well understood and produce the magnetism in ferrites and the ferroelectricity in piezoelectric oxides that make these materials so important. However, for non-stoichiometric compounds, and for stoichiometric compounds where thermally induced fluctuations produce effects analogous to those arising from impurities and dopants, the situation is very far from clear, and the puzzles are not merely academic. We are providing precise elasticity and thermal expansion data, important for the development of good theories of SPTs in heavily doped or fluctuating crystals, and crucial for a very broad spectrum of applications. This project has applications to thermoelectric converters, ceramics, semiconductors, materials testing, and the physics of condensed matter.

1. Background and Research Objectives

To understand the significance of this project, we begin by briefly reviewing second-order structural phase transitions (SPTs). We then describe recently detected failures of current theory, and why the failures exist.

A solid in thermal equilibrium rests at the minimum in the Gibbs free energy, G . To be concrete, we use as a paradigm the oxides, including the huge class of technologically important perovskites. For such systems, one has typically used as the independent variable of G a microscopic coordinate u describing the orientation of some structure formed by the oxygen atoms. This structure is typically rigid, with dynamics controlled by a non-parabolic

* Principal investigator, e-mail: migliori@lanl.gov

potential $V(u)$. Crystal symmetries often lead to a simple double minimum in $V(u)$. In the high-temperature (symmetric) phase of such systems, thermal population of $V(u)$ smears away the double well, producing a single minimum in G . As T is reduced, the system falls down $V(u)$ in a continuous way such that below the SPT transition temperature (T_S) the double minimum in $V(u)$ is reflected in G , whereupon the system undergoes a second order phase transition into the low-temperature (unsymmetric) phase. Although this picture is simple and attractive, it can be misleading. In fact, the usual description of the phase transition in the La_2CuO_4 system where the O atoms form a nearly rigid octahedron is formulated with an order parameter u corresponding to the octahedron tilt angle away from the Cu-O plane. This model produces accurately measurable predictions for the temperature dependence of the six independent elastic moduli that are not borne out by experiment. The conflict is sufficiently general to indicate that no simple vector order parameter can ever describe this system and, in fact, tensor order must be introduced. This is a new and important result.

Because of the tensor nature of elasticity, accurate measurements of the relative values of the elastic moduli through an SPT provide the most rigorous tests of theory, and in fact, are the only measurements capable of extracting the failures of simple treatments of the SPT. More important, and unlike the specific heat or thermal expansion, the elastic moduli play a unique role in theoretical treatments because the strains can couple to the order parameter. Thus the simple mean-field, or Ginsburg-Landau (G-L) Hamiltonian for second-order phase transitions always has strain/order-parameter coupling terms. Symmetry constraints determine the relevant exponents in the coupling terms, and those exponents in turn determine what happens to the elastic moduli.

In the above outline of the theoretical approaches used to describe the SPT in La_2CuO_4 and other SPTs, each model makes specific predictions about the temperature dependence of all the elastic moduli. Precision resonant ultrasound spectroscopy (RUS) measurements can measure the dependencies, thereby sorting out the theories. What we have found is that if only specific heat or thermal expansion is measured, simple vector order parameters work well enough. But once a tensor measurement is made (RUS) it is found that no combination of vector terms can satisfy the crystal symmetry and agree with the measurements. Thus at least quadrupolar order must be invoked. Much of the body of data available on other SPTs is missing full elasticity studies, producing similarly incomplete models. For example, in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, a Curie-Weiss (C-W) temperature dependence of the elastic moduli c_{33} and c_{66} begins an order of magnitude higher in $T-T_S$ than predicted by fluctuation theory, and its form is not understood using a vector order parameter. Without comparative data on the other moduli, no accurate test of a model can be made because many possibilities exist.

The so-called soft-mode-driven SPT just described for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ occurs in sensor and structural ceramic materials used throughout LANL programs and in minerals such as Fosterite and Olivine, crucial to propagation of nuclear seismic disturbances in the earth's crust. Because the phase transitions can be broader than predicted by simpler models, mechanical properties are degraded over large temperature ranges. Fundamental understanding of this degradation will benefit LANL advanced structural materials and sensor programs, and treaty verification. Technology transfer of the measurement approaches to private industry (QUATRO Corp.) has been achieved. Additionally, joint experiments with the GM Research Laboratory for the study of magnetoelastic effects near phase transitions in the $(\text{RE})_2\text{Fe}_{14}\text{B}$ permanent magnets and phase transitions in structural steel alloys have produced new results valuable for advances in manufacturing processes.

Our objectives were to understand order parameters and the coupling of electronic states to moduli in non-stoichiometric and stoichiometric systems undergoing structural phase transitions and the effects on mechanical or phonon (modulus) properties of other systems near regions of thermally induced changes in electronic states, and to use this understanding to extend fluctuation theories and theories of SPTs.

We have previously studied order parameters and coupling of electronic and structural contributions to the free energy of non-stoichiometric and stoichiometric systems including FeSi, YUPd_3 , $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, SrTiO_3 , CeRu_2 , and other materials by making detailed quantitative RUS and thermal expansion measurements, and obtaining full elastic constant data where good single crystals were available. We also studied the perovskite phase transitions by constructing Monte Carlo models that, though phenomenological, began to reproduce some of the more difficult-to-understand features of the RUS data.

2. Importance to LANL's Science and Technology Base and National R&D Needs

The Los Alamos RUS capability is unique. It provides the highest absolute accuracy of any modulus measurement system and can be used on the smallest (and therefore highest quality) single crystals of any ultrasound technique. This technique was developed at LANL by the principal investigator for this project. It is the only dynamic modulus measurement system generally available at the Laboratory, as is our precision capacitance dilatometer. These two tools are essential at any laboratory studying new materials. This project supports a Laboratory core competency in nuclear and advanced materials.

3. Scientific Approach and Results to Date

Our objectives were to understand order parameters and the coupling of electronic states to moduli in non-stoichiometric and stoichiometric systems undergoing structural phase transitions and the effects on mechanical or phonon (modulus) properties of other systems near regions of thermally induced changes in electronic states, and to use this understanding to extend fluctuation theories and theories of SPTs. To achieve these objectives, several series of RUS and thermal expansion measurements on very high quality dopable single crystals must be made. The systems important to this study include cubic dopable non-oxides with no SPT but with some reasonably large thermal expansion coefficient associated with an internal electronic energy scale comparable to accessible thermal energies, and tetragonal or higher symmetry dopable oxides with accessible SPTs. Because no one has had as yet the capability to observe relative modulus changes with the extreme precision of RUS, sample quality is more important than any other material property. For example, FeSi and Ce₃Bi₄Pt₃ are produced by us at LANL. Both of these small-gap semiconductors with Kondo lattice behavior have very sharp (high-Q) resonances, no SPTs, relatively large thermal expansion coefficients associated with the Kondo system, and are easy to dope. Their value here is that they lack any soft phonon modes, and thus the physics should be controlled by the small-gap energy scale interacting with thermal energy. Thus they are reasonably close to ideal systems for determination of the accuracy with which RUS measurements can extract free-energy details.

The systems of most interest are those with an SPT, especially those where the SPT clearly plays a fundamental role in other important physics. Here La_{1.875-x}Nd_xSr_{0.125}CuO₄ is ideal. This high temperature superconductor is of special interest because it has two SPTs in the region of temperatures accessible to RUS, an orthorhombic-to-tetragonal (OT) transition and a low-temperature tetragonal (LTT) transition. Both transitions are similar to the ones already studied, and both appear to strongly influence superconductivity. This material and the closely related but undoped compound La₂CuO₄ have been grown by us as large single crystals. Unfortunately, the crystals were so flawed that no RUS data could be obtained.

Nevertheless, other, though less ideal materials were available and were measured. RUS measurements were made of moduli, backed with capacitance dilatometer measurements of thermal expansion, in doped systems without SPTs but with a small energy scale (i.e. comparable to thermal energy scales accessible to us) such as FeSi, and in doped systems with SPTs including La_{2-x}Sr_xCuO₄. We looked at the shape and width of the transitions. Comparison of all moduli, and thermal expansion studies on the same samples used for modulus measurements provided a quantitative measure of modulus variation in simple and

SPT-containing systems. In the course of these measurements, we obtained all the elastic moduli of some of these systems over the temperature ranges of interest. Such information is not available from any other source for most of the materials chosen, and is of great value for molecular dynamical and structural modeling. Some of our accomplishments include:

- The discovery that a more complex order parameter was required to understand what was thought to be a simple soft-mode transition $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.
- RUS and/or thermal expansion measurements on FeSi , CoSi , SmB_6 , LaB_6 , U_2Zn_{17} , UCu_5 , CeRh_2Ge_2 , CeRu_2Ge_2 , EuB_6 , CuGeO_3 , Be-Zr-Ti-Ni-Cu amorphous alloys, $\text{YNi}_2\text{B}_2\text{C}$ and related compounds, YUPd_3 , YbInCu_4 , YbAgCu_4 and other materials. Many of the measurements discovered new phase transitions or new properties.
- Implementation of a 6T magnet capability for RUS and thermal expansion, and an RUS system capable of operation at 650 K.
- Construction of a Czochralski crystal puller.
- Production of samples of single crystals of many materials for ourselves, others in LANL, and around the world. These included undoped La_2CuO_4 untwinned single crystals on which we made full elastic constant measurements at temperature above 600 K.

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