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The research project entitled "Effect of Point Defects and Disorder on Structural Phase Transitions" was funded by the US Department of Energy through the Basic Energy Sciences Division (Ceramics Program) from 9/86 to 10/95, for a total amount of \$286,514. Annual reports were submitted every year and two renewal proposals were also submitted over the duration of the project. A special presentation on the project achievements was given in Washington in May of 1993 (Enclosure 1).

As a direct result of the work performed under the above contract, 18 papers were published in refereed journals, 19 contributed papers, 3 invited papers and several seminars were presented (Enclosure 2).

With regard to students, the project resulted in 3 PhDs (one did not actually graduate due to illness), all three now employed, and enabled 6 other students (3 graduate and 3 undergraduate) to participate in special research projects (Enclosure 3).

Although funding of this project by DOE has ended, the scientific work is nevertheless continuing through a collaboration that we initiated with the University of Le Mans (France) three years ago as an off-spring of the project.

Enclosure 1

**Effect of Point Defects and Disorder on
Structural Phase Transitions**

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Project Overview

Since the beginning in 1986, the object of this project has been Structural Phase Transitions (SPT) in real as opposed to ideal materials. The first stage of the study has been centered around the role of Point Defects in SPT's. Our intent was to use the previous knowledge we had acquired in the study of point defects in non-transforming insulators and apply it to the study of point defects in insulators undergoing phase transitions.

In non-transforming insulators, point defects, in low concentrations, marginally affect the bulk properties of the host. It is nevertheless possible by resonance or relaxation methods to study the point defects themselves via their local motion. In transforming solids, however, close to a phase transition, atomic motions become correlated over very large distances; there, even point defects far removed from one another can undergo correlated motions which may strongly affect the transition behavior of the host. Near a structural transition, the elastic properties will be most strongly affected so as to either raise or decrease the transition temperature, prevent the transition from taking place altogether, or simply modify its nature and the microstructure or domain structure of the resulting phase. One of the well known practical examples is calcium-stabilized zirconia in which the high temperature cubic phase is stabilized at room temperature with greatly improved mechanical properties.

The project first focused on two families of systems, fluoroperovskites and tantalates, both with the perovskite structure but exhibiting two distinct types of elastic behavior near the transition (different soft vibrational modes, one of them ferroelectric). In the several cases studied, the point defects created by the doping were relaxing defects (*Li*, *Na*), i.e. they could occupy several equivalent positions within a unit cell, between which they could

reorient at high temperature. To these defects is associated an elastic quadrupole moment and an electric dipole moment. These have been shown to have the strongest effect on the dynamical properties and on the pretransitional behavior upon approaching the transition.

Initially concerned with low concentrations of defects, the program has now been expanded to higher concentrations, such that the normal behavior of the solid is modified and the collective behavior of the defects themselves becomes important. In this concentration range, defects can in fact induce a phase transition normally absent in the pure system. Another situation that we are also investigating is that in which the collective behavior of the defects is different and even opposed to the collective behavior of the host, both leading to separate phase transitions. This situation can result in structural disorder and new elastic properties.

Although the systems studied have been insulators so far, we have found interesting analogies between them and some metallic systems undergoing martensitic phase transitions which we have therefore begun to study also. More specifically, these analogies have to do with the precursor effects that are observed prior to the transition or the formation of "embryos" of the low temperature phase.

In summary, the objective of the project is to understand the mechanisms underlying structural phase transitions in real materials. Initially focused on the role of point defects in low concentrations, the project has broadened to include higher concentrations and defect-induced phase transitions. One of the primary features that has emerged from our study is the importance of precursor effects. A comparison of these effects in two families of perovskite insulators with similar effects observed in shape memory alloys has led us to undertake a study of martensitic phase transformations.

Experimental and Theoretical Approach

The primary strength of this experimental project is the combination of multiple techniques applied to the same crystal(s). It is indeed very difficult to prepare several doped or mixed crystals that are completely identical and, if carried in different laboratories, different types of measurements cannot easily be related to one another.

The experimental techniques that are used in our laboratory are:

Dielectrics (linear and nonlinear, dielectric constant, dielectric loss)

Electric polarization

Ultrasonics (second order and recently third order elastic constants)

Raman spectroscopy.

Two years ago the PI also became involved with neutron scattering experiments at Brookhaven National Laboratory.

Finally, a Russian theorist who has been in a Visiting position for the past two and a half years, has also collaborated to the present project. Having previously developed a random field theory, independently from our experiments, our collaboration has been very successful, resulting already in 4 publications.

Project Main Personnel

1. General

Over the last 6 years, three students and the Principal Investigator have been involved in this research. The status of the three students is as follows:

Rose Wang (1987-1991), PhD, October 1991

Post-Doctoral Research Associate 1991-1992

Xiao Qin Wang (1988-1991), was in the process of writing up his thesis when he became seriously ill and had to return to China. He is now attempting to come back in order to complete his degree.

Lee A. Knauss (1990-present), anticipated date of PhD, Spring 1994.

The PI is Jean Toulouse, at Lehigh since the fall of 1984 and presently an Associate Professor in the Physics Department.

More recently, a Russian many-body theorist, presently a visiting professor at Lehigh, has been contributing to our group and in particular to this DOE project, although not supported by it.

2. Detail Research Activities (Past & Present)

Rose Wang

Initiated the research project on tantalates and in particular studied $KTa_{1-x}Nb_xO_3$ (KTN). Her thesis included dielectric and ultrasonic measurements of the transition as a function of temperature and for different frequencies. In collaboration with another student, Lee A. Knauss, she also measured the polarization hysteresis loops in this system. These provided the original evidence the formation of precursor effects in KTN. Her dielectric measurements under an applied field revealed the existence of non-linear effects and their direct relationship to the precursor effects. Finally, her ultrasonic results have shown that the transition is characterized by a tetragonal distortion and that the precursor effects, sufficiently far from the transition, can be described in terms of dynamical fluctuations.

Lee A. Knauss

Set up the Polarization Measurement system and performed the experiments leading to

the observation of the precursor effects. These measurements, combined with the Raman measurements discussed below have been essential in identifying the nature of these effects, namely the formation of polar microregions many degrees above the transition. This work is continuing but has been taken over along with the dielectric work, by another student supported by ONR.

L.A. Knauss has also been setting up a new ultrasonics system designed to measure non-linear elastic properties near the martensitic phase transition of NiAl and more specifically 3d order elastic constants. These elastic non-linearities appear to be the analogue of the dielectric non-linearities in the mixed ferroelectrics. The actual experiments have now begun for waves propagating in different directions and as a function of temperature. Measurements of resistivity are also done in parallel in order to precisely locate the phase transition.

Xiao Qin Wang

Performed an ultrasonic study of structural change (transition?) taking place in the high T_c superconductor $YBa_2Cu_3O_7$ above 200K and established a correlation between the location of the attenuation maximum and the superconducting temperature for different oxygen concentrations. Performed extensive dielectric and ultrasonic measurements of $KZnF_3:Li$ and $KMnF_3:Li$. He identified the nature of the Li defect in these two systems. Characterized the dielectric behavior (thermal hysteresis) at the transition and the influence of the lithium impurities on the precursor clusters. His ultrasonic results revealed the relaxational dynamics of the precursor clusters and, again, the effect of the dopant impurities on these. Due to a serious illness, X.Q. Wang did not complete the final analysis of the ultrasonic results which we are now in the process of doing. He is also attempting to return

in order to participate in this process and write up his dissertation.

Additional Project Personnel

Although not supported by DOE, two other individuals have greatly contributed to the progress of this research.

Phil DiAntonio

Has performed extensive Raman scattering measurements which have also revealed the presence of precursor order in the form of polar microregions many degrees above the transition. The correlation of these measurements with the polarization measurements done by Lee A. Knauss has been essential in identifying these microregions, a first in this field (see Phys. Rev. Letter). The Raman measurements have also permitted to estimate the size of these regions.

Boris E. Vugmeister

Has contributed essential theoretical expertise to the interpretation of the Raman spectra and polarization results.

It is important to note that the Raman spectrometer used in the above experiments was partially paid for with DOE funds. Yet because of the small size of our DOE grant we were not able to support a student to work with the instrument. Instead P. DiAntonio had to be supported by an ONR grant. Furthermore, despite the very important contribution of B.E. Vugmeister to the program we have had no flexibility whatsoever to contribute to his support on our small DOE budget. A summer student had also begun a Raman study of the precursor order in $KMnF_3 \cdot Li$ and found it to be similar to that in KTN . Due to the lack of funds, however, we were not able to support this student and continue this specific study at

the time. The overall project still has much potential that has not been realized because of the size of the grant.

Summary of Project Output

Under the name of each participant and in the overview, we have already detailed the different aspects of the project and the results that have been obtained. Here we will only highlight more general conclusions and potential for applications.

Our study of the role of dopant impurities or defects near structural phase transitions has helped recognize the importance, and in certain cases the prevalence, of precursor order. In pure systems, this precursor order may be confined to a narrow temperature range near the SPT or limited in magnitude. In doped systems however, this precursor order may be magnified as is being shown by the results obtained. The influence of this precursor order is double. First, it greatly enhances the susceptibility, dielectric or elastic, giving rise, near the phase transition, to strong non-linear responses which may be of great interest in materials applications. Secondly, the precursor order can have a significant influence on the nature of the phase transition (1st vs. 2nd order or nucleation and growth type) and on the domain structure or nanostructure of the low temperature phase (e.g. modulated properties). Defects or dopant impurities can be used to control the precursor order.

Relevance to the DOE Mission

In view of the research topics listed in the DOE brochure ER-0483P on Materials Sciences Programs, our own research program appears to be in the main stream of the DOE

mission. It is concerned with the fundamental properties of materials and, through the study of phase transitions, with the structure-properties relationship. To illustrate how this program coincides with the DOE mission, we have selected, in the brochure mentioned above, several of the phenomena headings which could be used in describing the various aspects of our project:

Critical Phenomena, Order-Disorder, Phase Transformations

Martensitic Transformation and Transformation Toughening

Mechanical Properties and Behavior

Phonons

Point Defects

Superconductivity

In view of these headings or keywords, our program appears to be an integral part of the DOE mission.

Budget Required. 10

17. The Effect of the Lithium Defect on the 186°K Structural Phase Transition of $KMnF_3$, J. Toulouse, X.Q. Wang and J. Nouet, Proceedings of the 7th International Meeting on Ferroelectricity, (Saarbrucken, 1989), *Ferroelectrics* 104, 379 (1990).
18. Effect of a DC bias Field on the Ferroelectric Phase Transition of KTN, J. Toulouse and X.M. Wang, Proceedings of the 7th International Meeting on Ferroelectricity (Saarbrucken, 1989), *Ferroelectrics* 106, 255 (1990).
19. Ultrasonic Study of the Low Temperature Phase Transition in $YBa_2Cu_3O_{7-\delta}$ and Its Dependence on Oxygen Concentration, J. Toulouse, X.Q. Wang and D.J.L. Hong, *Phase Transitions B* 22II, 1 (1990).
20. Longitudinal Elastic Behavior of the Mixed Ferroelectric KTN, X.M. Wang and J. Toulouse and L.A. Boatner, *Ferroelectrics*, 112, 255 (1990).
21. Dielectric non-linearity and spontaneous polarization of KTN in the diffuse phase transition range, J. Toulouse, X.M. Wang and L.A. Knauss, *Phys. Rev. B* 43, 8297 (1991).
22. Dielectric and Raman study of short and long range order in KTN, P. DiAntonio, X.M. Wang, J. Toulouse, L.A. Boatner, *Ferroelectrics* 120, 107 (1991).
23. Fundamental Experiments and New Horizons in Ferroelectricity, J. Toulouse, M.I. Bell, K.A. Nelson, N. Dalal, *Ferroelectrics* 120, 1 (1991).
24. Off-Center Lithium in the Fluoperovskite, $KZnF_3$, J. Toulouse, X.Q. Wang and M. Rousseau, *Phys. Rev. B* 44, 6635 (1991-I).
25. Precursor Effects and Ferroelectric Macroregions in $KTa_{1-x}Nb_xO_3$ and $K_{1-y}Li_yTaO_3$, J. Toulouse, P. DiAntonio, B.E. Vugmeister, X.M. Wang and L.A. Knauss, *Phys. Rev. Lett.* 68, 232 (1992).
26. Dipole-glass Behavior of Lightly doped $KTa_{1-x}Nb_xO_3$, P.M. Gehring, H. Chou, S.M. Shapiro, J.A. Hriljac, D.A. Chen, D.E. Cox, J. Toulouse, D. Rytz, and L.A. Boatner, (to be published in *Phys. Rev. B*).
27. Ultrasonic Study of the Li-induced Structural Phase Transition in $K_{1-x}Li_xTaO_3$, P. Doussineau, Y. Farssi, C. Frenois, A. Levelut, K. McEnaney, J. Toulouse, and S. Ziolkiewicz, submitted to *Euro. Phys. Lett.*, June 1992.
28. Polar Fluctuations and First Order Raman Scattering in Highly Polarizable Crystals with Off-center Ions ($KTaO_3:Li,Nb$), P.

Enclosure 2

Published Papers

1. A Modified Version of the Phase Sensitive Technique for Measurements of Sound Velocity in Solids, J. Toulouse, Proceedings of the Ultrasonics Symposium, Oct. 1987, IEEE Catalog #87 CH2492.7, p. 407.
2. Automated system for relative sound velocity and ultrasonic attenuation measurements, J. Toulouse and C. Launay, *Rev.Sci. Instrum.* 59, 482 (1988).
3. Elastic Anomalies at the Cubic-Tetragonal Transition in KTN, J. Toulouse, X.M. Wang and L.A. Boatner, *Solid State Commun.* 68, 353 (1988).
4. Ultrasonic Evidence for a Structural Transition at 220°K in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\text{d}}$, J. Toulouse and X.M. Wang, *Phys. Rev. B* 38, 707 (1988).
5. The Effect of the Lithium Defect on the 186°K Structural Phase Transition of KMnF_3 , J. Toulouse, X.Q. Wang and J.Nouet, Proceedings of the 7th International Meeting on Ferroelectricity, (Saarbrucken, 1989), *Ferroelectrics* 104, 379 (1990).
6. Effect of a DC bias Field on the Ferroelectric Phase Transition of KTN, J. Toulouse and X.M. Wang, Proceedings of the 7th International Meeting on Ferroelectricity (Saarbrucken, 1989), *Ferroelectrics* 106, 255 (1990).
7. Ultrasonic Study of the Low Temperature Phase Transition in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\text{d}}$ and Its Dependence on Oxygen Concentration, J. Toulouse, X.Q. Wang and D.J.L. Hong, *Phase Transitions B* 22II, 1 (1990).
8. Longitudinal Elastic Behavior of the Mixed Ferroelectric KTN, X.M. Wang and J. Toulouse and L.A. Boatner, *Ferroelectrics*, 112, 255 (1990).
9. Dielectric non-linearity and spontaneous polarization of KTN in the diffuse phase transition range, J. Toulouse, X.M. Wang and L.A. Knauss, *Phys. Rev. B* 43, 8297 (1991).
10. Dielectric and Raman study of short and long range order in KTN, P. DiAntonio, X.M. Wang, J. Toulouse, L.A. Boatner, *Ferroelectrics* 120, 107 (1991).
11. Off-Center Lithium in the Fluoperovskite, KZnF_3 , J. Toulouse, X.Q. Wang and M. Rousseau, *Phys. Rev. B* 44, 6635 (1991-I).
12. Dipole-glass Behavior of Lightly doped $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$, P.M. Gehring, H. Chou, S.M. Shapiro, J.A. Hriljac, D.A. Chen, J. Toulouse, D. Rytz, and L.A. Boatner,

Phys. Rev. B, 46, 5116 (1992).

13. Anomalous Dispersion and Thermal Expansion in Lightly-Doped $KTa_{1-x}Nb_xO_3$, P.M. Gehring, H. Chou, S.M. Shapiro, J.A. Hriljac, D.A. Chen, J. Toulouse, D. Rytz, and L.A. Boatner, *Ferroelectrics* 150, 47 (1993).
14. Non-linear Dielectric Properties of $KTa_{1-x}Nb_xO_3$, X.M. Wang, B.E. Vugmeister and J. Toulouse, (Proceedings of the 8th International Symposium on Applications of Ferroelectrics, Sept. 1992, IEEE Catalog #92 CH3080-9, p. 179).
15. Ultrasonic Study of the Li-induced Structural Phase Transition in $K_{1-x}Li_xTaO_3$, P. Doussineau, Y. Farssi, C. Frenois, A. Levelut, K. McEnaney, J. Toulouse, and S. Ziólkiewicz, *Eur. Phys. Lett.* 21, 323 (1993).
16. Polar Fluctuations and First Order Raman Scattering in Highly Polarizable Crystals with Off-center Ions ($KTaO_3:Li,Nb$), P. DiAntonio, B.E. Vugmeister, J. Toulouse and L.A. Boatner, *Phys. Rev. B* 47, 5629 (1993).
17. Strophoidal Argand Diagram and the Distribution of Relaxation Times in $K_{1-x}Li_xTaO_3$, P. Doussineau, Y. Farssi, C. Frenois, A. Levelut, K. McEnaney, J. Toulouse and S. Ziólkiewicz, *Phys. Rev. Lett.* 70, 96 (1993).
18. Polarization Switching and Long-time Relaxation Effects Induced by Off-center Ions in $KTa_{1-x}Nb_xO_3$, and $K_{1-y}Li_yTaO_3$, L.A. Knauss, B.E. Vugmeister and J. Toulouse, *Ferroelectrics*, 157, 251 (1994).
19. Polarization Relaxation in Disordered Ferroelectrics, J. Toulouse, R. Pattnaik, L.A. Knauss, *Jurnal of Non-Crystalline Solids*, 172, 538 (1994).

Contributed Papers

1. A study of the Li-defect in the fluoperovskites $KZnF_3$ and $KMnF_3$, J. Toulouse and C. Launay, MRS Fall meeting (Boston 1986).
2. Ultrasonic Attenuation of $KMnF_3:Li$ near the 186°K Structural Phase Transition, J. Toulouse, C. Launay and J. Nouet, APS March meeting (New York 1987).
3. The Role of Niobium at the Cubic-Tetragonal Phase Transition in KTN, X.M. Wang, J. Toulouse and L.A. Boatner, APS March meeting (New York 1987).
4. A Modified Version of the Phase Sensitive Technique for Measurements of Absolute Sound Velocity in Solids, J. Toulouse, IEEE Ultrasonics Symposium (Denver, 1987).

5. Elastic Anomalies at the Cubic-Tetragonal Phase Transition in $KTa_{1-x}Nb_xO_3$,
X.M. Wang and J. Toulouse, APS March meeting (New Orleans, 1988).
6. Dependence of the Ultrasonic Sound Velocity on the Oxygen Content of $YBa_2Cu_3O_{7-d}$,
J. Toulouse, X.M. Wang and B. Keramati, APS March meeting (New Orleans, 1988).
7. Effect of a DC Bias Field on the Ferroelectric Phase Transition of $KTa_{1-x}Nb_xO_3$ with
 $x = 15.7\%$, J. Toulouse, X.M. Wang and L.A. Boatner, APS March meeting (St. Louis,
1989) and International Meeting on Ferroelectricity (Saarbrucken, Germany, Sept. 1989).
8. Dielectric Behavior of $KMnF_3:Li$ Near the 186K Transition: The Effect of Li Impurities,
APS March meeting (St. Louis, 1989) and International Meeting on Ferroelectricity
(Saarbrucken, Germany, Sept. 1989).
9. Dielectric Non-Linearity and Spontaneous Polarization of KTN in the Diffuse Transition
Range, Bull. Am. Phys. Soc.35, 470 (1990).
10. Soft Mode-related Ultrasonic Attenuation in $KMnF_3:Li$, Bull. Am. Phys. Soc., Vol. 37,
No. 1, p. 597 (1992).
11. Raman Study of Precursor Effects in Li-doped $KMnF_3$ near the 187K Phase Transition,
Bull. Am. Phys. Soc., Vol. 37, No. 1, p. 597 (1992).
12. Transitions de Phase Dans les verres orientationnels $K_{1-x}Li_xTaO_3$, Meeting of the French
Society of Physics, Sept. 1992.
13. Polarization Switching and Low Frequency Dielectric Dispersions in $KTa_{1-x}Nb_xO_3$,
Materials Research Society, Boston, Fall 1992.
14. Polarization switching and Long Time Relaxation Effects in $K_{1-x}Li_xTaO_3$
 $KTa_{1-x}Nb_xO_3$, International Meeting on Ferroelectricity, IMF8, Gaithersburg, MD,
August 1993.
15. Ultrasonic Measurements in the Mixed System $KTa_{1-x}Nb_xO_3$, IMF8, August 1993.
16. Polarization Dynamics of KLT: A Model for Relaxor Ferroelectrics, *ibid*, p. 311
17. Ultrasonic Study of Mixed Ferroelectrics in a DC bias field, *ibid*, p. 311.
18. Polarization Dynamics in Relaxor Ferroelectrics, ISAF, Penn State University, August 1994.
19. Polar Clusters and Non-Analytic Dielectric Response of KTN in the Pretransition Regime
Bull. Am. Phys. Soc. Vol. 40, No. 1, p. 589.

Invited Papers

1. Defauts Substitutionnels dipolaires desordonnes dans un systeme fortement (KTN, KLT), Conference on the Role of Defects on Structural Phase Transitions, Metz (France), Fall 1991, Transphase IV, Loctudy (France), May 1992 (Invited).
2. Long Time Relaxation and Frequency Dispersion in Mixed Ferroelectrics, 2nd International Discussion Meeting on Relaxation in Complex Systems, Alicante (Spain), July 1993 (Invited).
3. A Comprehensive Study of the Random Dipole Ferroelectrics, KTN and KLT, 8th International Meeting on Ferroelectricity, Gaithersburg, MD, August 1993 (Invited).

Seminars

1. Soft Modes and Structural Phase Transitions, Lehigh University, April 1988.
2. Defects: Probes of Dynamical Phenomena Near Structural Phase Transitions, Columbia University, New York, March 1990.
3. Point Defects and Fluctuations Near Structural Phase Transitions, Brookhaven National Laboratory, April 1990 and National Center for Physical Acoustics (University of Mississippi), May 1990.
4. Coexistence Ordre-Desordre dans les systemes mixtes fortement polarisables, CENG, Grenoble, March 1992; Universite du Maine, Le Mans, April 1992; Universite de Rennes, April 1992, Universite P. M. Curie, Paris, April 1992.
5. Orientational Dynamics and Phase Transitions in Disordered Ferroelectrics, Universities of Lille, Dijon and Montpellier, January 1995.
6. Collective Dynamics and Two-Step Transitions in Disordered Ferroelectrics, Argonne National Laboratory, May 1995.

Enclosure 3

Students

Graduates

Rose Wang
Xiao Qin Wang
Lee A. Knauss
Ed Ehrlacher
Hongquan She
Y. Yang

Graduation Date

Ph.D. 1991
Ph.D. 1992 (interrupted due to illness)
Ph.D. 1994
Phys. 491 Graduate Research Course, Summer 1988
Phys. 491 Graduate Research Course, Summer 1994
Spring 1993

Undergraduates

Beta Keramati
Edward Condon
Kevin Cox

Fall 1989
1986-1987
Research Experience for Undergraduates, Summer 1993