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**THE EFFECTS OF POINT DEFECTS AND COMPOSITION
ON STRUCTURAL PHASE TRANSITION:
1989-90 TECHNICAL REPORT**

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ABSTRACT

During the first three years of this project, we have concentrated our effort on three systems: $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$, $\text{KZnF}_3:\text{Li}$ and $\text{KMnF}_3:\text{Li}$. The initial goals of the study were i) to develop the necessary experimental capabilities, ii) to identify the nature of the defects, iii) to characterize the effect of these defects on the phase transition. These goals have been successfully reached and we now propose to pursue the present research along three lines.

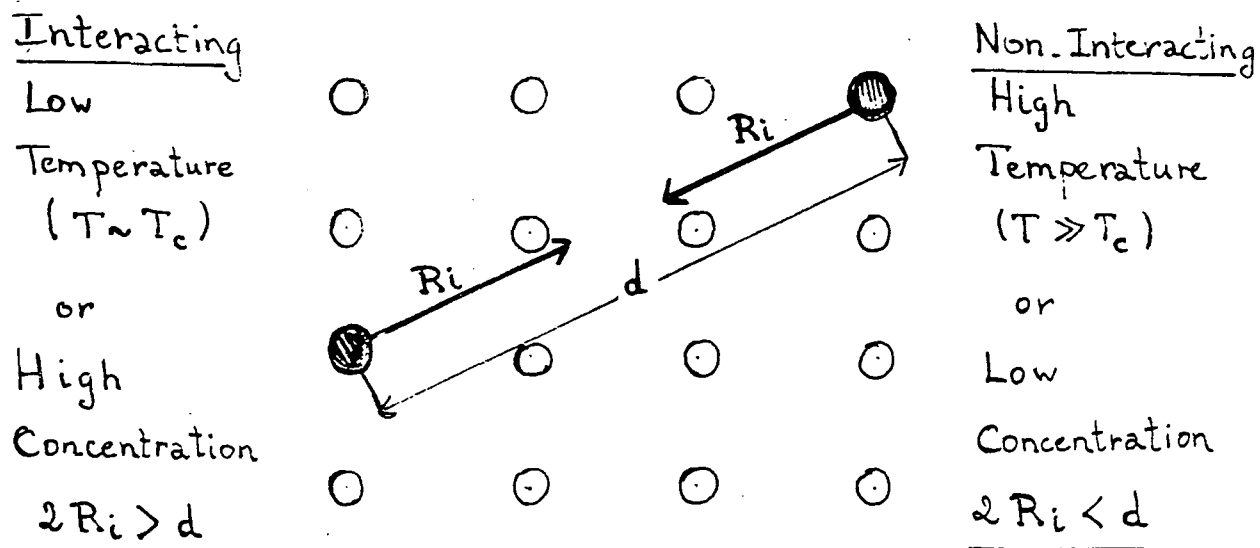
I. INTRODUCTION

Research in the field of structural phase transitions (SPT) and related critical phenomena has been rapidly expanding in the last fifteen years such that complete sessions are now devoted to the subject at major meetings. In the book entitled Physics Through the 1990's⁽¹⁾, two separate chapters are devoted respectively to "Structures and Vibrational Properties of Solids" and "Critical Phenomena and Phase Transitions". The early work has been, and quite understandably so, on nominally pure systems, but it has rapidly become clear that impurities, and the defect they form, can and do play an important role.⁽²⁾ Only recently have researchers started to systematically study the effects of defects and our previous proposal constitutes one of these early efforts.⁽³⁾ From another approach, a considerable interest has developed for mixed systems which can be viewed as containing large concentration of defects. These must then interact strongly with one another and with the "host" lattice.

We have just completed the third year of this research project. The research area of Structural Phase Transitions is entirely new to the Solid State Physics group at Lehigh. Within the last three years, we have therefore opened up a new field of research in which to train Lehigh physics graduate students. We have also introduced new experimental techniques in the Physics Department, such as ultrasonics, dielectrics and Raman spectroscopy. Our new effort in this area is also supported by a related effort in ferroelectrics in the Materials Science Department and an expansion of the Statistical Mechanics group of the Physics Department that can contribute to a better

understanding of critical phenomena in defective systems.

The general philosophy of the present proposal is illustrated in the diagram below. In this diagram we have



indicated the two most important defect parameters, namely the inter-defect separation, d , and the interaction distance, R_i , or the distance over which a defect can alter the surrounding medium. In contrast to "well-behaved" insulators, defects can have a determining influence on the bulk properties of "transforming" insulators near their SPT; this can happen when $2R_i$ becomes greater than d , a condition that can be satisfied at high concentrations (small d) or low temperatures close to the transition (large R_i).

The effect of defects will depend upon their nature and upon the origin of the prevailing interaction with the surrounding atoms.

II. RESULTS .

- SYSTEMS STUDIED

During the first three years of the present research, we have focused on three systems mentioned above because they are representative of the two major classes of soft modes, Zone Boundary and Zone Center. KZnF_3 and KMnF_3 are both fluoperovskites displaying a ZB mode. However, only KMnF_3 transforms, undergoing a cubic-to-tetragonal transition at 186.6°K . KZnF_3 being isostructural, and with an almost identical lattice parameter, is useful in determining the nature of the Li defect. KTaO_3 is an oxy-perovskite that does not undergo a phase transition until it is doped with Nb or Li. The transition temperature T_c is then directly related to the defect or impurity concentration. In this and the following pages, we report on the results obtained.

A. FLUOPEROVSKITES:

1. Defect Characterization

a) KZnF_3

•Dielectric loss peak \rightarrow Li off-center defect relaxing between crystallographically equivalent orientations with an activation energy of $E=0.12\text{eV}$.

b) KMnF_3

•No dielectric loss peak observed.

•ITC (Induced Thermal Current technique, also called TSDC or Thermally Stimulated Depolarization Current) \rightarrow no signs of Li dipole. Most probable explanation: the Li defect relaxation is frozen-in at the phase transition (microwave dielectric loss will be measured in collaboration with B. Golding of Bell Labs to verify this hypothesis).

2. Effect of Lithium on the phase transition of KMnF_3

a) Dielectric constant ϵ versus Temperature:

- observation of 3 ranges

• $(T-T_C) > 45K$: linear increase of ϵ with decreasing T independent of Li concentration \rightarrow intrinsic effect related to i) dynamical fluorine disorder (see Delye-Waller factors) or ii) limited softening of the ZC mode still present although not dominant.

• $(T-T_C) < 45K$: departure from the linear increase due to 2-dimensional fluctuations in the order parameter, here the rotation angle of fluorine octahedra. \rightarrow The effect of Li is to limit the amplitude of these fluctuations that goes as $c_{Li}^{1/3}$.

• Close to T_C , [$(T-T_C) < 10K$]: cross-over to 3-dimensional fluctuations, the amplitude of which also appears to be more limited as the Li concentration is increased.

b) Thermal hysteresis and transition temperature:

• As seen from the hysteresis loop in the dielectric constant, the transition is weakly first order. \rightarrow Li at low concentration reinforces the first order character of the transition.

• Li slightly shifts T_C to lower temperatures ($\sim 0.5K$ per 1000 ppm).

c) Ultrasonics:

• Sound velocity: in agreement with the dielectric measurements, Li is clearly seen to delay the transition and to reinforce its first order character at low concentration.

• Attenuation: the divergence in the attenuation observed near T_C for pure $KMnF_3$ is clearly reduced by the addition of Li. This is again consistent with the dielectric measurements showing a reduction of the initial fluctuations due to Li.

B. OXYPEROVSKITES:

1. Defect Characterization

a) KTN

•Nb in KTaO_3 substitutes for Ta. Below the ferroelectric (cubic-to-tetragonal) transition, a spontaneous polarization appears along a $\langle 100 \rangle$ direction.⁽⁵⁾ In accordance with the soft optic mode, this corresponds to an average displacement of Nb also along $\langle 100 \rangle$. However, there exists some experimental evidence indicating that Nb could be displaced along one of eight equivalent $\langle 111 \rangle$ orientations.⁽⁶⁾ Above T_c it would reorient between these eight positions, being on the average on center, while below T_c it would only reorient between only four of the initial eight positions, being on the average displaced along a $\langle 100 \rangle$ direction. Our own measurements are not conclusive yet on that point:

•Electron diffraction does not show any streaks, above or below T_c , that would indicate the presence of disorder in the position of Nb.⁽⁷⁾

•Ultrasonics: the velocity of transverse waves (C_{44} elastic constant) exhibits an anomaly starting at $T_c+25\text{K}$ that might be interpreted as signaling an off-centering of Nb at that temperature.

b) (K,Li) TaO_3 (not our results)

•Dielectric loss peak and polarization measurements $\rightarrow \langle 100 \rangle$ Li-off-center,⁽⁸⁾ activation energy $E=0.12\text{eV}$ which is the same as that we measured for Li in KZnF_3 .

2. Effect of Nb on the phase transition in $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$

a) Dielectric constant for three different concentrations

• Three transitions normally seen in simple perovskite ferroelectrics are observed. They are here induced by Nb.

• $T > T_c(C-T)$: Curie-Weiss behavior with departure below $T_c + 25K$

• ϵ peak measured at T_c with high ϵ_{max} and a width comparable to that reported for simple ferroelectrics \rightarrow Nb is homogeneously distributed throughout the crystals.

b) Spontaneous polarization P_s :

• Appearance of P_s at temperatures above T_c (ϵ_{max})

\rightarrow statistical distribution of Curie temperatures on a microscopic scale and diffuse character of the phase transition⁽⁹⁾ associated with Nb-induced disorder in $KTaO_3$.

c) Elastic constants

• Anomalous decrease in C_{11} above T_c with a $(T-T_c)^{-1}$ dependence \rightarrow coupling of the sound to polarization fluctuations (apparently with a 2-DIM character)⁽¹⁰⁾ due to the electrostrictive effect induced by the presence of Nb.

• Anomalous decrease in C_{44} in a narrower range of temperatures, starting at $T_c + 25K$ with $\ln(T-T_c)$ dependence \rightarrow may be due to either an off-centering of Nb at that temperature or alternatively related to the diffuse character of the transition.

• Field effect on both C_{11} and C_{44} \rightarrow characterization of the strong non-linearities introduced near the transition by the presence of Nb. The application of the field in different directions relative to the direction of propagation and polarization of the sound wave does suggest a displacement of Nb towards a $\langle 111 \rangle$ position at $T_c + 25K$.

3. Effect of Li on the phase transition in $K_{0.8}Li_{0.2}TaO_3$ (early results)

a) Elastic constant

•Anomalous decrease in C_{11} but smaller anomaly than in KTN and over a broader range of temperatures → Li induces a structural transition at ~133K which may have a different character than that observed in KTN (presence of ferroelectric microregions in a paraelectric matrix)⁽¹¹⁾ due possibly to a shorter interaction range, R_i , of the defects.

b) Raman spectroscopy

•Observation of normally forbidden first order Raman peaks above T_c is consistent with the presence of ferroelectric microregions continuously forming as T is decreased through T_c .⁽¹¹⁾

C. RESULTS SUMMARY

A very schematic summary of the results obtained is given in Table II below. Our specific contribution is underlined.

TABLE II

	NATURE OF THE DEFECT	EFFECT ON THE TRANSITION
KTaO ₃ WITH Nb	<u><111> OFF-CENTER</u> <u>Δ T ABOVE T_c</u>	<u>INDUCES TRANSITION:</u> DIPOLAR GLASS LOW CONC. <u>DIFFUSE TRANSITION</u> <u>AT INTERMEDIATE CONC.</u>
Li	<100> OFF-CENTER AT ALL TEMPERATURES	NORMAL FIRST ORDER AT HIGH CONC.
KZnF ₃	<u><110> OFF-CENTER</u>	<u>NO TRANSITION OBSERVED</u> <u>INTRINSIC 2.DIM FLUCTUATIONS</u>
KMnF ₃ WITH Li	<u>ALSO PRESUMED OFF-CENTER</u>	<u>AMPLITUDE LIMITED BY Li</u> <u>A ~ C_{Li}^{1/3}</u>

Although more work needs to be done to confirm certain of these results, the first three years of this program have reached the first set of goals chosen initially.

1) We have obtained conclusive information about the nature of the defects in the two families of systems studied.

2) We have identified the nature of the effect of these defects on the phase transition. In the ferroelectric KTaO_3 with Li and Nb, the soft mode is a zone center mode, due to the long range polar interactions. Defects in this case, initially limit the range of the interactions thereby introducing an element of disorder in the system. At very low concentration the transition has a "glassy" character while at intermediate concentration it becomes diffuse-ferroelectric. In the anti-ferroelastic KMnF_3 with Li, the soft mode is a zone boundary mode as a result of prevailing short range interactions. There, expectedly, the defect couples to fluctuations.

These results have been written or they are in the process of being written in the four articles which titles are listed below:

- Lithium defect in the fluoperovskites KZnF_3 , KMnF_3
- Dielectric anomaly and disorder at a non-ferroelectric transition: intrinsic versus extrinsic defects
- Elastic anomalies at the cubic-tetragonal transition in KTN
- Spontaneous polarization and dielectric non-linearity of KTN in the diffuse transition range