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Progress Report for June 15, 1988 - June 14, 1989

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RESULTS

During the first two years of the present research, we have focused on two systems representative of the two general classes mentioned above. $KMnF_3$ is a fluoperovskite that undergoes a cubic-to-tetragonal transition at $186.6^{o}K$. Here, this transition has been studied in Li-doped crystals. $KTaO_3$ is an oxyperovskite 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. These two systems are also representative of two separate types of phase transitions as will be explained below. This particular choice was made so as to be able to contrast the respective results obtained on the two systems and thus establish a general framework of reference.

A. Fluoperovskites

1. **Defect Characterization**

In our study of the effects of point defects on SPT's it is first important to characterize the defects. Lithium was chosen as an impurity because it is known to form an interesting "relaxing" defect pair in the chemically related rutile fluoride, MnF_2,[10] in which it also gives rise to structural instabilities.[11] In this latter system a lithium pair substitutes for Mn at the center of the distorted F_6 octahedron.

In order to characterize the Li defect, we chose to examine $KZnF_3$, another fluoperovskite with the same soft mode as $KMnF_3$ but in which no structural transition is observed. The results of dielectric loss measurements suggests that lithium at least partially, substitutes for potassium in one of several equivalent off-center positions (Fig. 1).[12] It is able to reorient between these positions that are separated by potential barriers of ~0.12 eV. A similar situation has been reported in $KTaO_3$:Li.[13] Similar dielectric measurements have been performed on $KMnF_3$ doped with the same lithium concentration but have failed to reveal any peak. ITC, or thermally stimulated depolarization measurements, have also been performed to extend the frequency or shift the temperature range in which the Li relaxation could be detected but did not reveal any peak either.[12] These results may actually suggest that, in $KMnF_3$, as in MnF_2, a lithium pair substitutes for Mn, thus forming an electrically neutral defect. It is interesting to note in this respect that several perovskite systems containing Li, such as $LiBaF_3$, actually possess an inverse perovskite structure in which Li occupies the center of the F_6 octahedron, normally occupied by the divalent metal cation.[14]

2. Coupling to the Soft Mode

The next step in the study has been to investigate the effect that the Li defect may have on the soft mode. As was mentioned earlier, $KZnF_3$ exhibits a soft transverse acoustic mode that is similar to that found in $KMnF_3$. Our measurements of the elastic constants C_{11} and C_{44} (respectively from longitudinal and transverse sound waves) in a crystal doped with 490 ppm Li also suggest a slight softening. These measurements are now being repeated in a crystal with a different Li concentration.

3. Li in $KMnF_3$: Changes in the Phase Transition

Several different types of measurements have been made on $KMnF_3$ pure and doped with 0.08%, 0.13% and 0.8% Li.

- Sound velocity (elastic constants) and attenuation (Figs. 2 and 3).

Measurements of the sound velocity in these crystals reveal a definite effect of lithium on the elastic behavior of $KMnF_3$. The presence of lithium shifts the anomalous softening of the elastic constant towards lower temperatures and changes the shape of the curve. These two observations may be interpreted as a shift in T_c as well as a change in the nature of the transition (from slightly first order to second order).

Similar effects of Li on the transition can be observed in the attenuation measurements. The attenuation increases initially at the approach of the transition and, already in pure $KMnF_3$, exhibits a peak that appears to shift towards higher temperatures as the sound wave frequency is increased. Such an observation is normally the sign of a relaxation and indicates the existence even above T_c of long-lived spatial fluctuations in the order of the system and the partial order-disorder character of an otherwise displacive transition. In agreement with the sound velocity measurements, the presence of lithium causes the attenuation peak to shift toward lower temperatures as well as to decrease in size. This may be interpreted as a reduction in the amplitude or in the extent of the spatial fluctuations.

M Dielectric constant

It is known from early measurements that the transition in $KMnF_3$ is slightly first order. In order to ascertain the degree of first order of the transition with and without lithium, as well as determine precisely the transition temperature, we have made careful measurements of the dielectric constant from room temperature down, through the transition (Fig. 4).[15] At the transition the dielectric constant exhibits a thermal hysteresis with a lower value of the constant below the transition than above it. At low concentrations, lithium enhances the first order character of the transition and shifts T_c down by over $1^{\circ}K$. At higher concentrations lithium depresses the first order of the transition and begins to shift T_c back up.

In the course of this work we were indirectly associated with measurements of inelastic diffuse neutron scattering on $KMnF_3$:Ca. These measurements were made in the close vicinity of the transition and demonstrated the existence of a critical slowing down of the atomic motions and the very long time it takes for the system to attain thermal equilibrium (up to 30 mn for a large crystal, after the temperature has been stabilized). Since then we have repeated the dielectric measurements reported above such that they are now reproducible. The elastic measurements will have to be similarly repeated.

B. Oxyperovskites: $KTa_{1-x}Nb_xO_3$ (KTN)

1. **Defect Characterization**

Niobium in $KTaO_3$ is known to substitute for tantalum. Below the cubic-to-tetragonal transition which is ferroelectric, a spontaneous polarization appears along a [100] direction. In accordance with the soft optic mode, this corresponds to an average displacement of the niobium also along [100]. There is some experimental evidence, however, that indicates that Nb could be displaced instead along one of the [111] directions; above T_c it would then reorient between 8 equivalent positions, being, on the average, on center (cubic site) while below T_c it would reorient between 4 equivalent positions, being, on the average, displaced along a [100] direction (tetragonal site).[16]

2. **Cubic-to-Tetragonal Transition**

- Dielectric[17]

Because this structural transition is also ferroelectric, we have used low frequency dielectric constant measurements (1) to precisely locate the transition temperature, T_C; (2) to measure the static critical exponent that contains information about the nature of the transition.

(a) The dielectric constant, ϵ, exhibits a sharp peak at T_C, the height of which appears to decrease with increasing frequencies (Fig. 5).

(b) A plot of ϵ^{-1} (Fig. 6) yields a straight line on both sides of the transition, a characteristic sign of a mean-field behavior in which the interaction between defects can be approximated by an homogeneous average field. It is interesting to note, however, that the two straight lines, respectively on the high and low temperature sides of the transition do not intersect the temperature axis at the same point which is normally the sign of a first order transition.

• Spontaneous Polarization[17]

An advantage of studying SPT's in ferroelectrics is the ease with which one can measure the other parameter of the transition, normally taken to be the spontaneous polarization. The measurements have been performed at different maximum fields and clearly reveal the main cubic-to-tetragonal SPT's as well as the two lower transitions (Fig. 7). Here again it is interesting to note that a non-zero spontaneous polarization persists at temperatures above T_C. This may be related to the observation made about the dielectric constant and suggests the existence of a metastable ordered (and ferroelectric) state which can be induced by an electric field above T_c.

• Elastic Constants[18] (see paper attached)

Extensive measurement of the sound velocity in a particular sample with x = 15.8% have revealed meaningful information.

The elastic constant C_{11} exhibits a sharp drop of about 35% upon approaching T_c from above. This drop can be attributed to a coupling between the sound wave and polarization induced by it, and which grows near the transition due to the divergence of the dielectric constant. Surprisingly, the elastic constant C_{44} also exhibits a sharp drop of about 4% and in a range of temperatures that is closer to T_c than for the C_{11} drop. The C_{11} drop is believed to be due to a coupling between the soft transverse optic mode and the transverse acoustic mode that is excited by the sound wave, a coupling presumably mediated by the off-centering of niobium. Results on the C_{44} constant appear to contain crucial information as to the role of niobium on the phase transition and which may explain the observation made earlier about the dielectric constant and the spontaneous polarization. A logarithmic plot of the anomalous part of the elastic constants also allows an estimate of the dynamical exponents that characterize the dimensionality of the atomic motions leading to the transitions: atomic motions in our 15.8% sample thus appears to be correlated in a plane down to a certain temperature $T > T_c$ while earlier measurements reported on a 28% sample indicated 3-dimensional correlations. Measurement of crystals with different Nb concentrations is therefore of utmost importance.

• Bias Electric Field

The above measurements of sound velocities or elastic constants have also been performed in the presence of bias electric fields of different magnitudes. These directly influence the transition temperature as well as, apparently, the dimensionality discussed above.

C. Results: Conclusion

The initial philosophy of this program has been to perform a variety of different measurements on a few crystals in order to characterize the transitions to be studied and identify their important features. In this first phase the analysis of the data has been mostly qualitative or only quantitative at an elementary level. We have identified, for instance, linear or logarithmic temperature dependences and estimated coefficients but have not yet attempted detailed fitting of experimental curves to theoretical models.

In both systems studied, $KMnF_3$ and $KTaO_3$, the respective defects, Li and Nb, have a significant effect on the phase transition. In $KMnF_3$, lithium modifies an existing transition, while in $KTaO_3$ niobium induces a transition that would otherwise not take place. The static effects of defects in both systems are to shift T_c on the one hand, and modify the order and the nature of the transition on the other hand. Dynamically, defects cause changes in the spatial extent and in the