Extrinsic Peak in the Susceptibility of Incipient Ferroelectric $KTaO_3$:Li

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Dielectric-constant measurements on $KTaO_3$:Li as a function of Li concentration, temperature, and frequency reveal the presence of a peak in the susceptibility near the paraelectric anomaly at 0 K. This effect is attributed to Li impurities which are "frozen" in an off-center position at the potassium site. For samples with a Li concentration of less than 24%, continuity of the elastic compliance ensures that a lattice polarization does not occur as for a true ferroelectric. Our results support the mean-field approach to the dynamics of impurities in ferroelectric hosts.

The initial observation of a "central peak"[1] in neutron scattering from $SrTiO_3$ provided a stimulus for the ensuing formulation of a number of theoretical models[2] whose purpose was to account for the associated low-frequency dynamics in certain phase transitions. A number of these models relates the scattering at a frequency $\omega = 0$ to the interaction between a slowly relaxing (or static) impurity mode[3,4] and a soft phonon mode. Theories of this type are apparently capable of not only accounting for the extreme narrowness characteristic of many observed central peaks, but also of predicting a shift of the transition temperature T_c which is positive when the defect is relaxaing and negative when it is static. Additionally it has been possible to predict, at least formally, the deviations of the response of an impure system from that of a pure system.[5] Nevertheless, while this approach is obviously able to account for a number of features observed experimentally, a full validation in a test system where the impurity if fully identified and its properties are known is still lacking.[6]

The purpose of this Letter is to present a means of testing the validity of the mean-field approach to low-frequency dynamics by measurements of the central-peak response in a system where the responsible impurity is identified and its concentration is controlled.

Displacive-type ferroelectrics are particularly simple systems whose response function, as represented by the dielectric constant, allows a peak centered at $\omega = 0$ to be resolved with an accuracy of $\Delta\omega \approx 1$ Hz. From numerous possible examples of such systems, $KTaO_3$:Li was selected since lithium has been previously[7] identified in this host by infrared absorption and its posi-

tion in the lattice was determined as being "off center." The Li impurity is in a substitutional site for potassium and couples linearly to the order parameter which, in this case, is represented by the polarization. Since the lithium ion is off center, it may occupy any one of several equivalent positions and can hop between these positions with an Arrhenius frequency of $v = v_0 \times \exp(-\Delta/kT)$, where Δ represents the potential barrier height separating equivalent positions. Infrared data have shown that $v_0 \approx 1.2 \times 10^{12}$ Hz. Depending on whether the hopping frequency v were above or below the frequency of observation the lithium would represent a "relaxing" or "frozen" defect. These conditions are exactly those required by the current theoretical explanation of the dynamical susceptibility of impurities near a phase transition.

In order to investigate the dynamics of the Li impurity, its complex dielectric response has been measured as a function of observation frequency, sample temperature, and lithium concentration. Figure 1 shows the resulting Cole-Cole plots obtained by plotting ϵ'' versus ϵ' at a constant temperature for a sample with a lithium concentration of about 1.2%. Here the observation frequency is a parameter which increases along the curve in going from right to left, and each curve is labeled by its corresponding temperature. From similar determinations of the dielectric response for samples with varying concentrations of lithium, it is possible to show that the dielectric dispersion [i.e., $\epsilon(f \sim \infty) - \epsilon(f = 0)$] is proportional to the lithium concentration below 1.2% Li. Additionally, a polarization can be frozen in by cooling the sample from above 30 K to 4 K with a dc bias of about 2×10^5 V/m. The
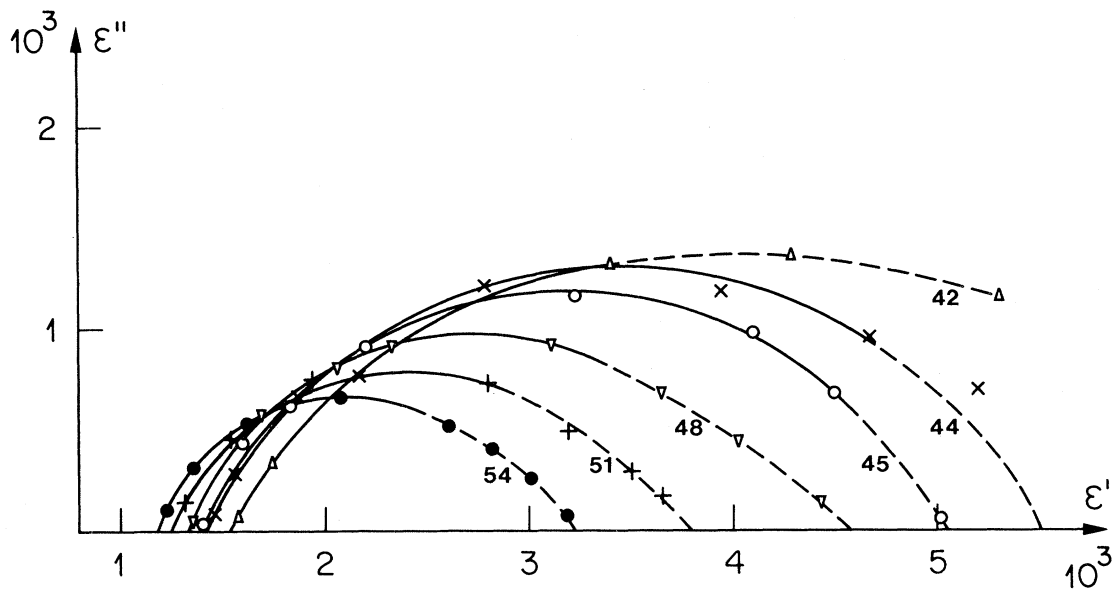

FIG. 1. Imaginary part vs real part of the dielectric constant as a function of frequency for several labeled temperatures (Cole-Cole plots). The lithium concentration is 1.2%.

polarization is a continuous function of the Li concentration and is about twice as large $\vec{E} \parallel \langle 100 \rangle$ as for $\vec{E} \parallel \langle 111 \rangle$. The cumulative results show that the Li impurity is responsible for the dielectric dispersion observed and are consistent with a $\langle 100 \rangle$ off-center direction. The frequency at which ϵ'' is a maximum is identified as the hopping rate of the Li between equivalent $\langle 100 \rangle$ positions. From the Arrhenius plot shown in Fig. 2 the oscillation frequency may be determined as

$$\log_{10} v_0 = 11.8 \pm 1.$$

This is in good agreement with the value of 1.2×10^{12} Hz determined from the infrared measurements.[7] Additionally a value of $\Delta = 0.125$ eV is found for the barrier height. Also, we can be seen from Fig. 2, the transition from dynamic to static behavior occurs at about 25 K as defined by a slowing down of the response below 10^{-4} Hz. Recalling that the sample is still paraelectric at this temperature, it is possible, in this case, to classify the lithium as a frozen-in impurity of Halperin-Varma type A2. The response of the system including Li may then be identified as $\epsilon(0)$, and that of the pure lattice (the phonon response) as $\epsilon(\infty)$. These responses have been obtained from Cole-Cole plots at several Li concentrations, and their inverse is plotted in Fig. 3. It is immediately apparent that the total response $[\chi_t(q_0)]^{-1}$ not only falls below the phonon response $[\chi_l(q_0)]^{-1}$, but also below that of pure $KTaO_3$ (i.e.,

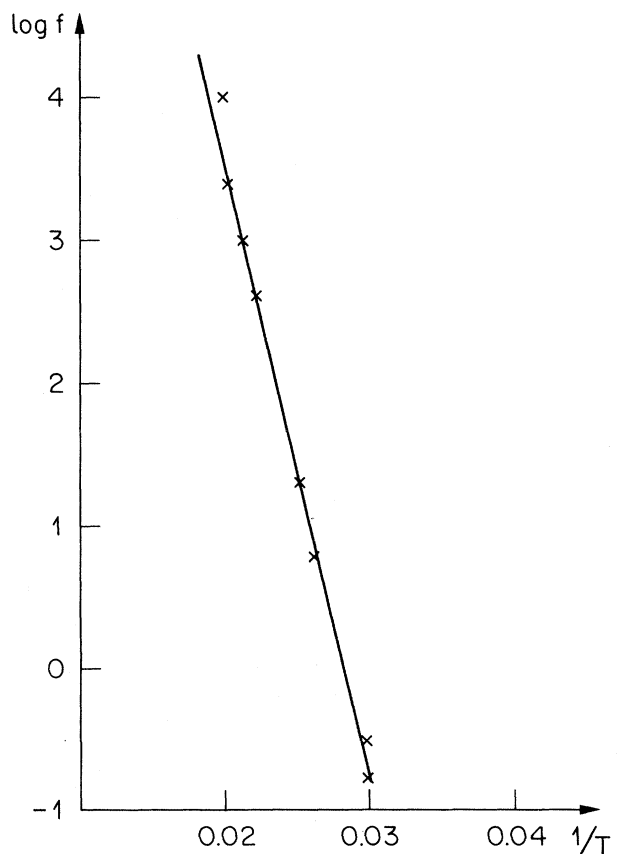FIG. 2. Arrhenius plot of $\log f$ vs $1/T$ with f the frequency of maximum dielectric loss. ($\log f_0 = 11.8 \pm 1.0$, $\Delta = 0.125$ eV.)
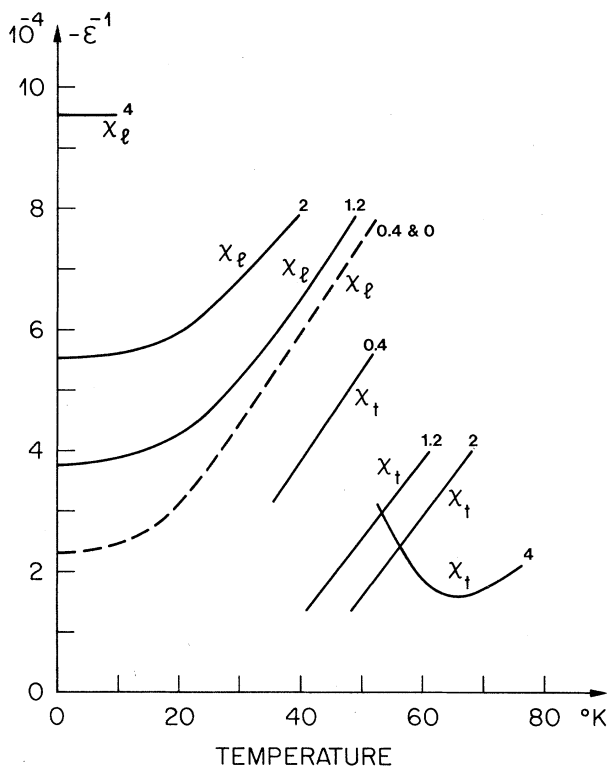
FIG. 3. Total response χ_t and *lattice* response χ_l of KTaO$_3$:Li as a function of temperature. Note the resemblance to the qualitative predictions displayed in Fig. 3 of Ref. 3.
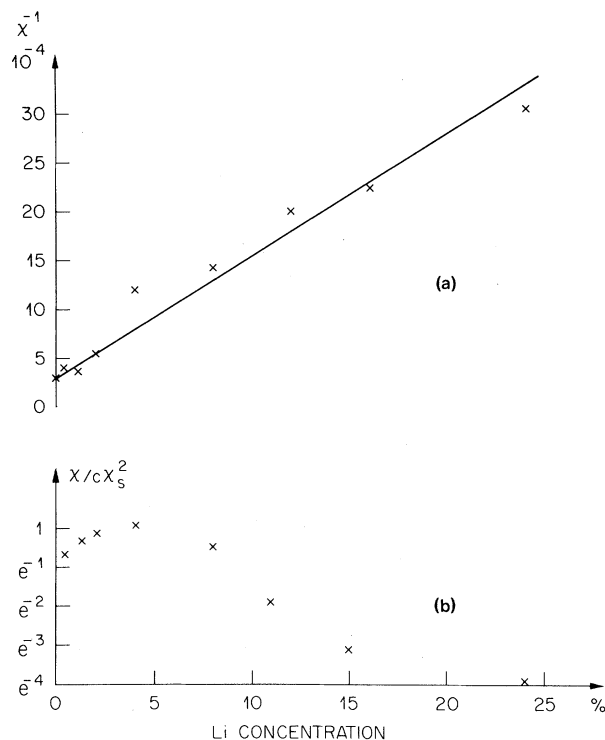

FIG. 4 (a) Susceptibility of KTaO$_3$:Li at 0 K. Spontaneous polarization $P_s = 0$. Note that ϵ^{-1} increases almost linearly with the Li concentration which is consistent with the suppression of ferroelectric order by Li impurities. Experimental error is less than 10^{-3}; scatter is due to inhomogeneity of samples. (b) Normalized dynamic susceptibility $\chi/c\chi_s^2$ on a log scale. For isolated impurities, $c \leq 8\%$, $\chi/c\chi_s^2 =$ const within a factor of 2.

$[\chi_0(q_0)]^{-1}$. At finite temperatures, $\partial\chi^{-1}/\partial T$ is the same for all three curves and corresponds closely to the inverse Curie constant of the pure system. The coincidence of $\partial\chi/\partial T$ for the three curves outside the critical region is evidence for a slight change of the long-range forces due to the incorporation of Li impurities. In the critical region, at $T < 40$ K, χ(Li) diverges for low Li concentration and this is evidence for the static nature of the Li polarization at this temperature.

Since quantum-mechanical fluctuations are known to suppress ferroelectric order[8] in KTaO$_3$, the actual transition temperature and its shift cannot be measured directly. Instead one may use the 0-K dielectric susceptibility as a measure of the dipolar interaction, which is shown in Fig. 4 as a function of temperature. Apart from minor scatter which may be due to some sample inhomogeneity, the susceptibility decreases almost linearly. The remanent polarization was measured from the piezoelectric effect[9] induced by biasing the samples at 4 K for several minutes. It is below 10^{-5} C/m^2 for all samples of KTaO$_3$:Li, whereas for KTaO$_3$:Nb a true spon-

taneous polarization has been determined[10] to be 3×10^{-2} C/m^2 at a Nb concentration of 3%. In addition, the acoustic step anomaly reminiscent of a phase change in KTaO$_3$:Nb is completely lacking in KTaO$_3$:Li, $s_{11}^{-1}(4$ K$) = 3.85 \times 10^{11}$ N/m^2 for 1.2% and $s_{11}^{-1}(4$ K$) = 3.9 \times 10^{11}$ N/m^2 for pure KTaO$_3$; thus we conclude that $P_s = 0$. *The decrease of $\chi(0)$ with lithium concentration at $P_s = 0$ is clear evidence of the suppression of ferroelectric order by Li impurities.* This is in agreement with the recognition that frozen-in impurities enhance fluctuations[3] and thereby decrease the ferroelectric order and stability limit of the paraelectric phase. Even though the Li polarization may be frozen in by cooling the sample below a given temperature, measurements of the elastic compliance clearly show that a lattice polarization does not occur and, accordingly, that the material is not a ferroelectric in the usual sense.

For noninteracting impurities, the theory has been used to predict the weight of the central peak with the following result:

$$\chi(q) = \int S(q, \omega)\, d\omega = c(x_n/x_d)^2 J_0^2 \chi_s^2, \qquad (1)$$

which has been expressed in terms of the parameters of the pure system and the isolated impurity. Here x_n and x_d represent the linearized mean-field response of a normal (potassium) and a defect (lithium) site to its surroundings, and J_0 describes the nearest-neighbor interaction. Since x_n, x_d, and J_0 are model parameters independent of experimental conditions, Eq. (1) predicts that $\chi(q)/c\chi_s^2 = \text{const}$ for all concentrations c and temperatures. We show in Fig. 4(b) that for $\chi(q)$ and c varying over one and one-half orders of magnitude, $\chi(q)/c\chi_s^2$ varies by less than a factor of 2. This shows clearly that mean-field theory predicts reasonably well the weight of the central peak for noninteracting impurities. At concentrations above 8%, $\chi(q)/c\chi_s^2$ drops drastically to about 1/100 of its low-concentration value at a lithium content of 24%. In this concentration range the Cole-Cole plots become flattened and are indicative of an entire (nonlognormal) spectrum of hopping frequencies which are responsible for dielectric relaxation. This should give rise to a broadening of the central peak—an effect which might be resolved by neutron scattering. At a lithium concentration of 40%, the coupled Li modes apparently become soft, driving the crystal into a complicated ferroelectric structure of the tungsten-bronze type.[11]

The present results have shown that Li is an impurity which, when incorporated in the $KTaO_3$ host at concentrations below ~1%, is responsible for an extremely narrow (1 kHz) central peak. Its dynamic properties are correctly described by mean-field dynamics of a static impurity in a ferroelectric host. At higher concentrations the central peak is broadened and, above ~25 K, the transition between static and dynamic behavior occurs. $KTaO_3$:Li does not become ferroelectric at any temperature as long as the lithium concentration is less than 24% and the observed dielectric dispersion cannot be identified with a ferroelectric soft mode.

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Spin-Flip Scattering Time of a Spin-Glass

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We have used, for the first time, superconducting tunneling to study the magnetic ordering properties of a normal metal. We find that the spin-flip scattering time of a spin-glass increases markedly as the temperature is lowered through the temperature at which the susceptibility exhibits a cusp. The results are interpreted as a measurement of the temperature dependence of the spin-glass order parameter.

In order to elucidate the character of the spin-glass phase transition, we have undertaken extensive measurements of the temperature dependence of the conduction-electron spin-flip scattering time of AgMn, through the ordering temperature T_G, using an electron tunneling technique. We