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Dielectric and elastic-response investigations of polar motion in potassium-sodium tantalate

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Résumé. — L'instabilité polaire de $K_{1-x}Na_xTaO_3$ est associée à une variation critique des réponses linéaire et non linéaire. Les résultats sur les susceptibilités diélectriques et élastiques montrent un ralentissement critique de 10^9 à 10^7 Hz de l'oscillation des ions Ta^{5+} en s'approchant de la température critique. La polydispersion de la susceptibilité à basses fréquences et la divergence de la susceptibilité non linéaire sont des indications en faveur du gel d'une configuration désordonnée à une température légèrement inférieure à la température critique (extrapolée). Les modèles habituels des verres dilués n'expliquent pas cette quasi-coïncidence. Par contre, nous cherchons un scénario dans lequel les interactions de type ferroélectrique et les interactions frustrées entre les impuretés dipolaires sont accrues par la corrélation entre les distorsions dipolaires du réseau.

Abstract. — The polar instability of $K_{1-x}Na_xTaO_3$ is associated to critical linear and nonlinear phenomena. Data on linear dielectric and elastic susceptibilities show a critical slowing down from 10^9 to 10^7 Hz of the Ta^{5+} motion on approaching the critical temperature. Polydispersive susceptibility at low frequency and critical nonlinearity are evidence for freezing of a disordered configuration only slightly below the (extrapolated) critical temperature. Standard models of dilute glasses do not account for this near-coincidence. Instead, we search for a scenario in which both the ferroelectric and the frustrated interactions between impurity dipoles are enhanced by the critical correlation of lattice dipolar displacements.

1. Introduction.

Solid solutions of perovskite oxides are abundant [1] and of scientific [2] and technical interest [3]. Few of them have been thoroughly investigated, and the ones that have been show quite complex behaviour [4, 5]. Of the 16 simple perovskite oxides, the majority have a polar instability [1]. In particular $KTaO_3$, the host lattice of the crystals reported here, has a dielectric susceptibility which reaches 5×10^3 at 4 K. Associated to large susceptibilities is an enhanced correlation of polar motion [6]. Accordingly, in $KTaO_3$, impurities interact at larger distances [7] than in inert lattices like NaCl. The interaction between impurities in polarizable lattices has been the subject of a perturbation calculation [7]

and computer simulation [8]. Both approaches showed strong deviations from the familiar dipolar form when the impurities were closer than some critical distance r_c . The complexity of this interaction J_{ij} between dipoles p_i and p_j and its long range preclude a theoretical treatment of the Hamiltonian

$$\mathcal{H} = \sum J_{ij} p_i p_j. \quad (1)$$

In absence of reliable theoretical predictions, we attempt to gain experimental insight into the material in which such interactions between impurities in a polarizable lattice play a dominant role.

The system $K_{1-x}Na_xTaO_3$ (KNT) is a mixed perovskite oxide. It has been the subject of several studies [9-11] which attributed its polar phase the character of an ordered state. Some observations, however, are incompatible with the ferroelectric-like ordered nature of the low-temperature phase of KNT: There are no domain walls visible [12, 13] as

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in isostructural ferroelectric BaTiO₃, and the polarization cannot be switched [13] by electric fields E at temperatures T below the critical T_c . A search for the critical nuclear magnetic relaxation T_1 of ²³Na resulted in a report that T_1 was in fact continuous right through T_c [14]. The ensuing uncertainty regarding the nature of the transition leaving local properties unaffected prompted a re-investigation of collective phenomena [15] in KNT and associated compounds [16]. The main result was the discovery of two relaxation contributions. A high-frequency relaxation peak showed monodispersive character, independent of Na and Nb addition [16]. This relaxation was attributed to ordered Ta motion. A low-frequency relaxation phenomenon showed polydispersive character, dependent on Na content, and was associated to a glass transition. Both phenomena were observed in the same sample ($x = 0.2$) at neighbouring temperatures.

In this paper, we wish to present a completed investigation of dielectric relaxation and nonlinear susceptibility in five samples with Na content x ranging from 0.08 to 0.24. The data are supplemented by acoustic-resonance and Brillouin scattering measurements. The purpose of this paper is to correlate the seemingly independent order and disorder phenomena. In particular, we shall present clear evidence that nonlinear susceptibility is critical in the sense of a glass transition [17]. We point out that critical linear and nonlinear susceptibilities are related in the x - T phase diagram. This relation calls for a common origin for the two phenomena which we shall propose at the end.

2. Experimental results.

A previous investigation on the nonlinear dielectric susceptibility in $K_{1-x}Na_xTaO_3$ concentrated on the sample with $x = 0.2$ [15]. While it established the existence of a glass phase, it did not attempt to dwell on the origin of the interactions leading to a glassy state. In this section, we expand the previous investigation to samples with different Na concentrations. Furthermore, we present dynamical results on the elastic compliance on the same sample, and finally we intend to correlate the different results in a qualitative way.

2.1 STATIC NONLINEAR SUSCEPTIBILITY. — We present the coefficient ε_{NL} , called nonlinear susceptibility and defined by

$$\varepsilon_s(E, T) = \varepsilon_s(0, T) - \varepsilon_{NL}(T) E^2 + (O)(E^4). \quad (2)$$

Here ε_s denotes the static susceptibility, measured in fact at $f = 1$ kHz to obtain optimum precision. The inability to measure ε_s directly forces us to exclude data obtained in a low-frequency dispersive regime. These data fall into a temperature range around T_g . Lowering the measuring frequency to, say, 10 Hz

would be of little help in approaching T_g in view of the slow algebraic dispersion [15] of the imaginary part of the dielectric susceptibility $\varepsilon_2 \sim \omega^\nu$, $\nu \sim 0.1$, there. Data of $\varepsilon_s(E, T)$ have been fitted to equation (2) in a standard way [18]. The result for ε_{NL} is plotted in figure 1 as a function of temperature for five different samples. The analysis in terms of the scaling function [18] $a(T) = \varepsilon_{NL}(T)/T\varepsilon_{lin}^4$ yields the dashed curves also shown in the figure. According to this analysis, which is identical to that of [15] and [18], a divergence of $a(T)$ of the form $a \sim (T - T_g)^{-\gamma}$ indicates a transition to a glassy state provided $T_g > 0$. Inspection of figure 1 indicates that $T_g < 0$ for 8 % and ~ 0 for 12 %. We find $T_g = 5$ and 11 K for 16 % and 20 % Na doping, respectively. No divergence of $a(T)$ is indicated for 24 % Na doping.

Fig. 1. — Nonlinear dielectric susceptibility data $\partial\varepsilon/\partial(E^2)$, scaling functions $a(T) = \text{const. } \varepsilon_{NL}/(T\varepsilon^4)$ vs. temperature fitted to $[(T - T_g)/T]^{-\gamma}$. The samples are those used in an earlier investigation [11].

2.2 DIELECTRIC DISPERSION. — At sufficiently low temperatures, the samples with 16 % Na and 20 % Na reported earlier [15] are dispersive. The results of $\varepsilon_2(\omega)$ for 16 % Na doping are plotted on log-log scale in figure 2. The fit to straight lines indicates that $\varepsilon_2 = A\omega^\nu$, and the parameters are shown in figure 3. We note that below about 15 K the amount of dispersion given by A rises sharply. In this temperature range, measurement of the dynamical nonlinear dispersion [19] is a nontrivial matter not attempted here. Other samples show only negligible low-frequency dispersion.

2.3 ELASTIC COMPLIANCE. — A small electric bias (of 10^3 V/m) is sufficient to render $KTaO_3$ piezoelectric. Such samples resonate at a frequency f_r [20]. Real and imaginary parts of the elastic compliance

Fig. 2. — Imaginary part of the audio-frequency dielectric susceptibility vs. ω in log-log representation. Straight lines: $\varepsilon_2 = A(T) \omega^{\nu(T)}$.

Fig. 3. — Parameters A and ν vs. temperature (see Fig. 1 or Eq. (1)). Note that ν is maximum at T_g and A vanishes above T_g .

are obtained from the resonance frequencies f_∞ (far away from dispersion regimes) and f_r (in the dispersion regime) and from their width Δf_r as

$$\text{Re}(s) - s_\infty = (f_\infty^{-2} - f_r^{-2})(4l^2\rho)^{-1} \quad (3)$$

$$\text{Im}(s) = \Delta f_r f_r^{-1}(f_\infty^{-2} - f_r^{-2})(4l^2\rho)^{-1}. \quad (4)$$

Here s_∞ is the elastic compliance s_{11} above the dispersion regime, l and ρ are the length (5.9 mm) and the mass density (7000 kg/m³) of the sample. Equations (3) and (4) hold for a long thin sample vibrating in length extension, l being parallel to the x -axis of the crystal. We plot the real part of the critical elastic compliance vs. T for $x = 0.2$ in figure 4. It shows the same smeared-out step function as found previously [11] and an x -dependent step for all other samples with $x \geq 0.12$. Evaluation of the resonance data in terms of a Debye-type monodispersion yields

$$s_\infty - s = \Delta s / (1 + j\omega\tau), \quad (5)$$

where τ is the relaxation time of the strain. We have plotted the relaxation time of the local quadrupoles [21], $t_q^{-1} = 6\tau^{-1}$, vs. temperature in figure 5. We find $10^7 \text{ s}^{-1} < \tau^{-1} < 2 \times 10^8 \text{ s}^{-1}$. On lowering T ,

Fig. 4. — Elastic compliance of $\text{K}_{0.8}\text{Na}_{0.2}\text{TaO}_3$ vs. temperature. For comparison, scaling function $a(T)$ (see Fig. 1) and square of linear susceptibility adjusted to scale at 25 K.

τ^{-1} drops to its lowest value of 10^7 s^{-1} at $\sim 13 \text{ K}$, and below 13 K it stays constant.

We have also investigated acoustic relaxation in presence of a field: in figure 6 we plot τ_q^{-1} vs.

Fig. 5. — Dielectric and acoustic relaxation rates vs. temperature, $\text{K}_{0.8}\text{Na}_{0.2}\text{TaO}_3$.

Fig. 6. — Acoustic and dielectric relaxation rates vs. field, $\text{K}_{0.8}\text{Na}_{0.2}\text{TaO}_3$.

E at different temperatures, again for $x = 0.20$. Moderate fields of a few kV/m are able to slow down relaxation by an order of magnitude.

2.4 BRILLOUIN SCATTERING. — Measurements were performed using the 514.5 nm line of a single-mode Argon laser and a double-pass Fabry-Pérot interferometer with a free spectral range of 60 GHz. The right-angle scattering configuration was used ; the incident and scattered beams were perpendicular to the [100] faces of the samples, so that the acoustic phonons selected were propagating along the (110) direction. The polarization of the incident light was normal to the plane of scattering. Two phonon peaks were attributed to a longitudinal and a shear mode ; their elastic constants are $1/2(C_{11} + C_{12} + 2 C_{44})$ and C_{44} , respectively.

The variations of the frequency shifts *versus* temperature are plotted in figure 7. The accuracy of the measurements is about 1 %. We note that the Brillouin shifts vary by less than $\sim 2\%$ with temperature, even at T_g . Thus, the relaxation rates must be below $\nu_L / \sqrt{0.02} \sim 5 \times 10^9$ Hz, in agreement with elastic data.

Fig. 7. — Brillouin shift due to longitudinal (upper curve) and transverse (lower curve) acoustic waves while lowering (Δ) and increasing ($\blacklozenge$) T .

2.5 SUMMARY OF EXPERIMENTAL RESULTS. — Critical nonlinear susceptibility and algebraic dispersion of the linear susceptibility are associated to a glass transition [17], whereas critical linear susceptibility and Debye dispersion arise in a ferroelectric-type order-disorder transition [2]. Thus, not all our observations have a common origin, yet they occur under identical conditions, namely for $x > x_c$ and near the (x -dependent) T_g . In the following, we attempt to explain these puzzling features.

3. Interpretation.

In this section, we wish to describe the critical behaviour of the susceptibility and compliance in terms of models which have been advanced in connection with phase transformations.

We recall that the linear dielectric susceptibility follows a Curie-Weiss type behavior

$$\varepsilon_{\text{lin}} \sim (T - T_c)^{-\gamma},$$

where T_c depends on concentration as $T_c = A(x - x_c)^{1/2}$, $x_c = 0.12$, $A = 60$. The exponent γ depends on T_c (and thus on x) ; for $T_c = 0$ it approaches the value of 2, and for larger T_c it takes the Curie-Weiss limit $\gamma = 1$. In the most thoroughly investigated sample, $x = 0.2$, $T_c = 11$ K, $\gamma = 1.4$. The rise of the exponent γ [10] is attributed to quantum-statistical fluctuations of the polarization arising from soft modes with frequencies $\omega > kT_c/\hbar$ [22, 23]. Accordingly, one expects the onset of a spontaneous macroscopic polarization below T_c , a divergence of the susceptibility on both sides of T_c and a nonlinear susceptibility $\varepsilon_{\text{NL}} \sim \varepsilon_{\text{lin}}^4$. Experiments show that no macroscopic polarization arises spontaneously ; ε_{lin} does not diverge below T_c [15], but the renormalized nonlinear susceptibility $\varepsilon_{\text{NL}}/\varepsilon_{\text{lin}}^4$ does diverge. These findings are contrary to expectations from ferroelectric models, but exactly analogous results have been reported in spin glasses [17] and explained in terms of the model by Sherrington and Kirkpatrick (SK) [24]. They assume that the interaction J_{ij} between species i and j is a random variable with a variance $\left\{ \sum_{i,j} (J_{ij} - \bar{J}_{ij})^2 \right\}^{1/2}$ exceeding its average $J_0 = \bar{J}_{ij}$.

The only random variables in KNT are the dipolar interactions between random-site off-center [25, 26] Na ions at K sites. It is natural to identify them as J_{ij} of the SK model (Eq. (1)).

We start by estimating the polar displacements and their correlations of Ta and Na dipolar orientations in KNT. From the remanent polarization [13], $P = 12$ mc/m², it follows that $p_{\text{Ta}} \sim 7.7 \times 10^{-31}$ Cm, which corresponds to a displacement $\delta_{\text{Ta}} \sim 0.01$ Å. This compares to $\delta_{\text{Na}} \sim 0.04$ Å as obtained from magnetic-resonance data [26] on the nuclear spin of ²³Na in KNT. In view of the dilution and the lesser charge, the contribution of Na ions to P can be neglected, and it follows that the direct interaction between random-site Na dipoles must be much weaker than the Ta-Ta interaction. Yet, the Na dipoles appear to determine the disordered character of KNT below T_c . The correlation length ξ of the fluctuating dipoles may be estimated from the static susceptibility. If coherent regions of size $\xi^3 = n \times d^3$ (n = number of dipoles, d = lattice constant) are considered independent of one another, then the fluctuations of their dipole mo-

ments np_{Ta} will give rise to a susceptibility of the order of

$$\varepsilon = (N/n)(np_{\text{Ta}})^2/3 kT\varepsilon_0. \quad (6)$$

Here, N is the total number of dipoles, N/n the number of coherent regions, and $\varepsilon_0 = 8.85 \text{ C/Vm}$ the conversion factor in SI units. We find $n = 1.5 \times 10^5$ and $\xi \sim 200 \text{ \AA}$ for $x = 0.2$. This is several orders of magnitude smaller than the domain size in isostructural ferroelectric BaTiO_3 .

According to random-interaction models, the non-linear susceptibility ε_{NL} should diverge more strongly than $\varepsilon_{\text{lin}}^4$ [18]. The function $a(T) \equiv \varepsilon_{\text{NL}}/T\varepsilon_{\text{lin}}^4 \sim (T - T_g)^{-\gamma_{\text{NL}}}$, which is a measure for the divergence of the spin-glass susceptibility [17], is plotted in figure 4. We find $\gamma_{\text{NL}} = 1.5, 2.0$ and 1.7 for $x = 0.12, 0.16$ and 0.2 , respectively. These findings are analogous to those on CuMn [17], and both results are compatible with the Sherrington-Kirkpatrick version of a glass. For $x = 0.08$, the divergence of $a(T)$ falls into the negative temperature range. We may call this sample an *incipient glass* in analogy to the incipient ferroelectric. No divergence of $a(T)$ is found for $x = 0.24$. This sample, which shows a very broad maximum of ε_{lin} with respect to T , may have compositional inhomogeneities on a macroscopic scale.

From a dynamical treatment of the SK model, it was concluded [27] that the polarization decayed as $P \sim t^{-\alpha}$, and accordingly the imaginary part of the dielectric susceptibility behaved as $\varepsilon_2 = A\omega^\nu$, with A nonzero below T_g and $\nu \sim 1/2 - (T - T_g)/\pi T_g$. As for the sample with $x = 0.2$ [15], this behaviour was tested for $x = 0.16$ (see Fig. 2). Again, it appears that ν is overestimated, a fact attributed to the use of mean-field theory [28]. The samples with 0.24 and 0.12 are only weakly dispersive and not suited for a quantitative analysis. No dispersion is reported for $x \leq 0.08$.

The critical elastic compliance originates from the coupling of the strain to the polarization. In non-piezoelectric perovskite structure, this coupling [29] is of the form $S \times P^2$, S being the strain. Accordingly, the elastic compliance gives a measure of the correlation of four polar units. Are these units the ordered Ta dipoles or the disordered Na dipoles? Coupling between ordered dipoles leads to the relation $s \sim \varepsilon_{\text{lin}}^2$ when treated in mean-field theory [29]. We have plotted $\varepsilon_{\text{lin}}^2$ vs. T in figure 4, adjusting the scale at 25 K . The fit to $s \sim \varepsilon_{\text{lin}}^2$ is not convincing. We also note that in distinction to ordered SrTiO_3 [30], at fit of $s(T)$ to $|T - T_c|^{-\mu}$ on both sides of T_c is not possible. Thus, there are no critical fluctuations of the local quadrupole moments near T_c . Correlation between four *disordered* dipoles is described by the scaling function $a(T)$. This function (Fig. 4) does not fit the data of $s(T)$ either.

While static scaling arguments fail to elucidate the origin of the elastic anomaly, considerations on the dynamical behavior are more suggestive. In the critical temperature range, ε_{lin} is dispersive as $(1 + j\omega\tau)^{-1}$, i.e., of Debye type for $\omega \geq 10^5 \text{ Hz}$, and as ω^ν , i.e., algebraic for $\omega \leq 10^5 \text{ Hz}$. For ultrasonic dispersion, only very few data points are usually available. We concentrate on our resonance data taken at $3 \times 10^5 \text{ Hz}$ and postulate that, in analogy to the dielectric data, these data be explained by monodispersion. As a result, we find the true static value for the elastic compliance which practically coincides with the values at $3 \times 10^5 \text{ Hz}$ (Fig. 5). In addition, we determine the relaxation time of the strain τ_s^{-1} , and by considering the channels through which relaxation can occur [20], we find $\tau_q^{-1} = \tau_s^{-1}/6$, where q indicates a local quadrupolar distortion. The result for τ_d and τ_q is plotted in figure 5: both τ_d and τ_q slow down critically and have nearly the same value, $\tau^{-1} \sim 2 \times 10^7 \text{ s}^{-1}$ at T_g . The small step in the acoustic phonons measured by Brillouin scattering at $5 \times 10^9 \text{ Hz}$ is in agreement with the value of τ_d and τ_q deduced from ultrasonic resonance data.

The motion of the dipoles has been attributed to Ta^{5+} ions earlier [16]. Since the elastic quadrupoles have the same time scale in the entire critical region, those quadrupoles and thus the elastic anomaly measured at $3 \times 10^5 \text{ Hz}$, are associated to ordered motion of Ta^{5+} . Our data do not provide evidence for or against arithmetic elastic dispersion as predicted for spin glasses [31]. On approaching T_c , we find that both the linear dielectric and elastic susceptibilities start diverging, a precursory sign for the onset of ordering. Rather than exhibiting a range of criticality (like $s \sim |T - T_c|^{-\nu}$), they are both stabilized at some finite value, indicating that no long-range order is established. At about the same temperature, and in the same samples, critical nonlinearity and arithmetic dispersion occur; these effects are attributed to a freezing-in of a disordered polar configuration. The ferroelectric interactions $\bar{J}_{ji}$ and the spin-glass interactions $\text{var}(J_{ij})$ must therefore be of the same order of magnitude. While conceptually appealing, it is not possible to attribute $\bar{J}_{ij}$ to the strong ferroelectric Ta-Ta interaction and $\text{var}(J_{ij})$ to the weak random Na-Na interaction: instead we wish to describe a scenario of polar freezing in KNT which, admittedly, is speculative.

We start by recalling that collective polar phenomena in perovskite oxides are commonly attributed to the nonlinear polarizability of the oxygen ions [32]. This leads to attraction between Ta and O in linear chains. The attraction is enhanced by Nb substituting for Ta, leading to a condensation of an ordered polar mode. Since Na, substituting K, is not at the proper position to enhance the Ta-O

attraction, the enhancement of polar interactions due to Na addition must have a different origin.

We propose that the oxygen polarizability is enhanced through structural relaxation. When 20 % Na ($r_{\text{Na}} = 0.95 \text{ \AA}$) substitute for K ($r_{\text{K}} = 1.34 \text{ \AA}$), the occupied volume per unit cell shrinks by 2.5 %. The total unit-cell volume, however, shrinks by only 0.75 % [1], $d(0) = 3.99 \text{ \AA}$, $d(0.2) = 3.98 \text{ \AA}$. Accordingly, more space is available for the oxygen to deform. Upon lowering the temperature or increasing Na content, the motion of the Ta becomes more and more correlated and stronger. At the same time, the coupling between Ta and off-center Na is enhanced. This leads to an effective interaction between Na dipoles which is enhanced when x increases. In the language of the SK model [23], where the probability for interaction J is

$$p(J) = \exp - [(J - J_0)/\Delta J]^2,$$

both the average interaction J_0 and its variance ΔJ are a function of x (or of T when x is constant). Simultaneous growth of J_0 and ΔJ with x explains why disorder phenomena, such as critical nonlinear susceptibility and hierarchical relaxation [27], occur under the same conditions as ordering phenomena, such as diverging linear susceptibility and elastic compliance as well as critical slowing down. It also calls for caution when comparing data with results of the SK theory which considers J_0 and ΔJ temperature-independent and of infinite range. True dipolar interactions in real crystals and particularly in KNT do not belong into this category. They have dipolar character only for large distances $r > r_c$, whereas for $r < r_c$ there are strong deviations: self-consistent model calculation suggests that below r_c the randomness ΔJ is considerably enhanced [8]. On the other hand, coupling between dipolar orientation and polar lattice modes adds an effective ferroelectric component [7] to J_0 . Thus, the growth

of r_c near T_c simultaneously drives the growth of both J_0 and ΔJ , the parameters which govern linear and nonlinear susceptibility, respectively. The result of a model calculation of dipolar interactions might render this suggestion less speculative.

4. Conclusions.

The linear susceptibility and the elastic compliance are critical near a temperature T_c which depends on the Na concentration of (K-Na)TaO₃. They are monodispersive in the same frequency region; this indicates that a quadrupolar deformation follows the polar displacement of Ta adiabatically. Below T_c , the linear susceptibility has a constant value of 3×10^4 from which we deduce a correlation volume of the polar displacement of 1.5×10^5 unit cells. This corresponds to 200 Å linear dimension. Finite correlation, critical nonlinear susceptibility, and hierarchical relaxation are trademarks of a transition to a glassy state. They involve disordered polar motion attributed to off-center random-site Na ions.

Ordered motion of Ta and disordered motion are strikingly correlated. They occur in samples with Na concentration $x \geq 0.12$ and, there, in the neighborhood of the x -dependent critical temperature. We argue that the enhancement of the ferroelectric-type interaction between Ta ions at lattice sites is due to the volume gain for the polarizable oxygen ion arising from substitution of K⁺ by the small Na⁺ ion. Enhanced ferroelectric interaction entails enhanced polarizability of the lattice, and this triggers an increase of the interaction between impurity Na dipoles. This interaction is frustrated, i.e., it can be attractive or repulsive according to the ion pair considered. It is this enhanced frustrated interaction that ultimately leads to the formation of a dipolar glass state. This state is characterized by hierarchical relaxation evidenced by arithmetic dispersion in the low-frequency range, and a diverging nonlinear static susceptibility.

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