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Calorimetric Investigation of Clustering in $KTaO_3$-Based Compounds

S. Riegel, R. Wengenmayr, and G. Weber
Institut für Festkörperphysik, Technische Hochschule, D-W 6100 Darmstadt, Germany

U. T. Höchli
IBM Research Division, Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

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Heat-capacity and heat-release data are reported in $K_{1-x}Na_xTaO_3$ for $x=0$, 0.08, and 0.24 at temperatures below 1 K and attributed to reorientations of the nuclear quadrupoles of ^{181}Ta. In pure $KTaO_3$, the quadrupoles relax exponentially, whereas doping with Na at the K site introduces relaxation described by the Kohlrausch stretched-exponential function.

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Potassium tantalate is the prototype incipient ferroelectric. Its polarizability grows upon reduction of temperature T and reaches a maximum, $\varepsilon=4500$, at $T=0$. The large polarizability is connected to the collective motion of Ta ions with respect to their oxygen cages.[1] Their motion can be excited by an ac electric field up to 10^7 Hz; the average residence time of a Ta ion at an off-center site is accordingly about 10^{-8} s, the off-center distance being of the order of 0.04 Å.[2] Substitution of K ions by the isoelectronic impurities Na and Li retards the motion and introduces a new kind of nonlinear, extremely slow dynamics. In particular, Na has been shown to introduce history-dependent nuclear magnetic resonances (NMR),[3] to break polar correlation into microscopic lengths,[4] and to introduce dielectric dispersion in the audio-frequency regime.[5]

It has been suggested that even in pure $KTaO_3$, regions of coherent polarization of Ta ions should form, and that these regions, called clusters, should have near-static character.[6] Very slow responses, however, are difficult to measure, in particular in the presence of an enormous dynamic response. Attempts to detect low-frequency dielectric dispersion in pure $KTaO_3$ have, up to now, been unsuccessful and hence there is currently no way to determine the slow dynamics of pure and doped $KTaO_3$. NMR spectra do not resolve the quadrupole splitting; therefore, redistributions between energy levels cannot be deduced. We propose thus to present, for the first time, low-frequency calorimetric data on a quadrupole system and to deduce its dynamic structure from the thermal response.

The calorimeter was run in the semiadiabatic mode.[7] Its main feature was a weak thermal link consisting of NbTi wires between the sample and a base plate allowing heat release from the sample to be measured by thermometry.[8,9] The samples were single crystals of $K_{1-x}Na_xTaO_3$, with $x=0$, 0.08, and 0.24, and a mass of about 0.4 g each. They were grown with the spontaneous nucleation technique.[10]

The measuring procedure was as follows: The sample assembly was cooled to the base temperature T_b, typically 200 mK, at a rate of 3 mK/s. After remaining at T_b for two hours, the sample was heated within 10 s to an "initial temperature" T_i and left there for a holding time t_h. The heat was then allowed to flow back while the temperature drop from T_i to T_b was recorded as a function of time. Resolution was 1 pW.

For $x=0$, the heat-release curve dq/dt vs t can be described by the sum of two exponentials

$$dq/dt=k_A\exp(-t/\tau_A)+k_Q\exp(-t/\tau_Q)\,. \qquad (1)$$

The two terms indexed A and Q represent the short- and the long-term contributions of the heat release, respectively. Calibrations with a Cu sample and of the empty sample holder allowed identification of the two contribu-

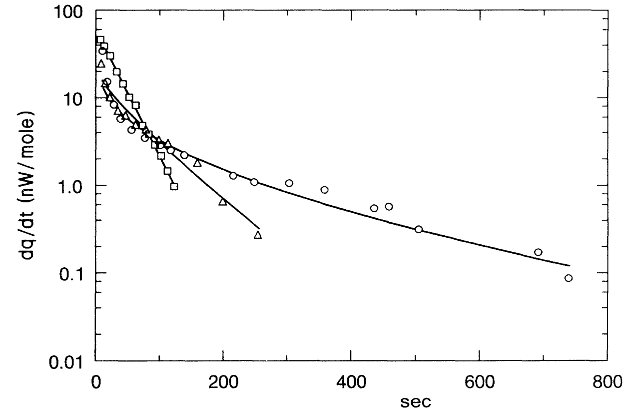

FIG. 1. Heat release dq/dt in nW/mole vs time for $K_{1-x}Na_xTaO_3$. □, $x=0$; △, $x=0.08$; ○, $x=0.24$. Temperature T_b is 200 mK. Temperatures T_i are 213, 224, and 224 mK for $x=0$, 0.08, and 0.24, respectively. Solid lines are fits of dq/dt by dK/dt, where $K(\Phi_0,\beta,\tau)$ is the Kohlrausch function (Ref. 12); see Eq. (4). Parameters are $\beta=0.99$, 0.96, 0.68; $\tau=31$, 60, 120 s for $x=0$, 0.08, and 0.24, respectively. The parameter values $\beta=0.99$ and 0.96 for $x=0$ and 0.08 imply that relaxation is very nearly exponential in these samples.

tions: The term in $\tau_A = 0.57$ s (at $T_b = 200$ mK) is instrumental; it includes the addenda and the rapidly decaying[11] phonon contribution c_{ph} of the sample. The second contribution is dominant after 10 s and allows the parameters k_Q and τ_Q to be evaluated. One example ($T_i = 213$ mK, $T_b = 200$ mK) of dq/dt vs t is shown in Fig. 1. It is readily established that this contribution exceeds that of the Debye heat capacity by 2 orders of magnitude.

An evaluation of the heat capacity corresponding to the second exponential $c_Q = (T_i - T_b)^{-1} \int (dq/dt) dt$ as a function of temperature T_b is given in Fig. 2. The heat capacity is expressed in terms of $c_Q = k_c T^{-\nu_c}$. Also in this figure are values for $\tau_Q = k_\tau T^{-\nu_\tau}$.

Thus we find that $c_Q \gg c_{\mathrm{ph}}$, that in good approximation $c_Q \propto T^{-2}$, and that $\tau_Q \propto T^{-2}$ (Fig. 2). This suggests that the pertinent energy levels are below $k_B T$ and that relaxation is driven by a two-phonon process. These are properties typical of a nuclear quadrupole system: We attempt thus to describe our heat data in terms of the well-known energy-level diagram of ^{181}Ta in a crystalline field. This nucleus possesses a spin I of $\frac{7}{2}$ and has 100% isotopic abundance. The $2I+1$ energy levels associated with it are Kramers degenerate in zero magnetic field. Electric-field gradients arising from the crystalline field split the levels $|M| = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$, and $\frac{7}{2}$ into states with energy 0, Δ, 3Δ, and 6Δ, respectively.[12]

The heat capacity derived from the partition function reads, for $T \gg \Delta/k_B$,

$$c_Q = 21 N \Delta^2 / 4 k_B T^2 . \tag{2}$$

A fit of the data in Fig. 2 by Eq. (3) determines $\Delta/k_B = 0.38$ mK. The field gradient V_{zz} at the site of the ^{181}Ta quadrupole vanishes for cubic symmetry. If the Ta ion is displaced with respect to its center position by an amount d, then $\Delta \propto d^2$ and we find

$$c_Q = \mathrm{const} \times T^{-2} d^4 , \tag{3a}$$

and, following Ref. 2,

$$\mathrm{const} = 1.562 \times 10^6 (1-\gamma)^2 N e^2 Q^2 / a^{10} k_B [2I(2I-1)]^2 \varepsilon_0^2 , \tag{3b}$$

with the Sternheimer factor $1-\gamma$, Avogadro number N, unit charge e, quadrupole moment Q, lattice constant a, nuclear spin I for ^{181}Ta, and $\varepsilon_0 = 8.85$ pF/m. Comparing Eqs. (3a) and (3b) with our experimental results we find $d = 0.053$ Å if d is single valued, and $\langle d^2 \rangle^{1/2} = 0.057$ Å for Gaussian-distributed d.

This value is compatible with that obtained by NMR spectroscopy.[2] In addition, the relaxation times shown in Fig. 2 are compatible with those extrapolated from high-temperature NMR measurements.[2] Since quadrupoles have inversion symmetry, relaxation implies 90°, rather than 180°, reorientation of the off-center Ta ion. Such 90° flips are rare, whereas 180° flips seen by dielectric measurements are frequent.[13]

Having identified the essential contributor to heat release, we are now in a position to study the influence of Na doping on quadrupolar relaxation. Doping with Na leads to nonexponential heat release as shown in Figs. 1 and 3, which can be described by the Kohlrausch[14] function $K(t)$:

$$dq/dt = dK/dt = \Phi_0 (t/\tau)^{\beta-1} \tau^{-1} \exp[-(t/\tau)^\beta] , \tag{4}$$

where τ is the relaxation parameter, $\beta - 1$ is a measure

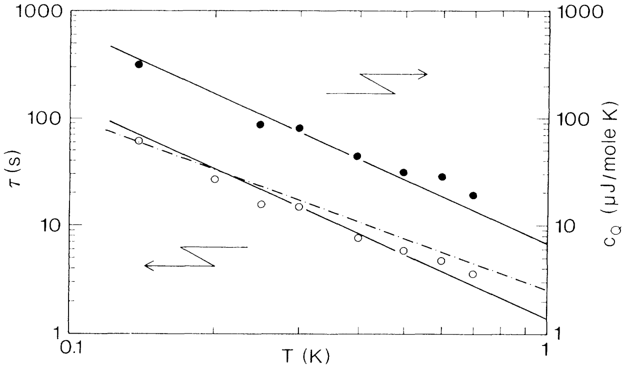

FIG. 2. Heat capacity c_Q and relaxation time τ_Q vs T. Solid lines indicate best fits by $c_Q = k_c T^{-\nu_c}$ and $\tau_Q = k_\tau T^{-\nu_\tau}$; $k_c = 7$ μJ/mole K, $k_\tau = 1.4$ s, $\nu_c = 1.92$, $\nu_\tau = 2.04$. Dash-dotted line indicates simultaneous fit of present data set and of NMR relaxation times taken above 5 K (see Ref. 2) by $\tau = k' T^{\nu'}$; $\nu' = 1.7$. Sample is $KTaO_3$.

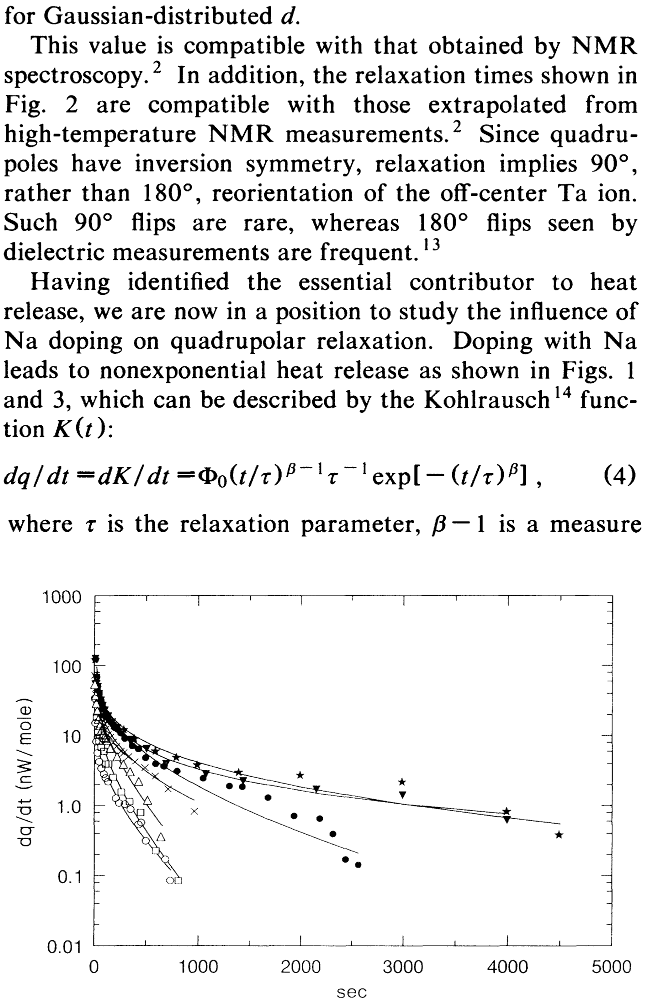

FIG. 3. Heat release dq/dt vs time for different heat pulses and holding times. Sample is $K_{0.76}Na_{0.24}TaO_3$. Temperature T_b is 200 mK. We give the heat pulse in terms of $T_i - T_b$ (mK), τ (s), and β for the first five curves with holding times of 10 min, starting at the left: ○, 24, 110, 0.68; □, 67, 80, 0.52; ★, 157, 110, 0.74; ●, 269, 180, 0.50; ×, 480, 260, 0.60. For the last curve, holding time was increased from 10 to 30 and 60 min, respectively: ▼, 480, 500, 0.6; △, 480, 3000, 0.46. The heat capacity $c_Q = \Phi_0/(T_i - T_b)$ was nearly independent of x and T_h. See also Fig. 2.

for nonexponentiality, and $\Phi_0/(T_i - T_b)$ is the heat capacity. We note that for pure $KTaO_3$, $\beta-1$ implies exponential decay, whereas for 8% Na and 24% Na doping the values are $\beta=0.96$ and 0.68, respectively, see Fig. 1.

Deviations from exponential decay have been regarded as evidence for hierarchical relaxation.[15,16] To test this concept we have measured the heat release as a function of heat input and holding time and fitted the results by dK/dt (Fig. 3). We note that the parameter τ increases if the heat pulse and/or the holding time is increased, whereas β is about 0.5 for $x=0.24$. For 8% doping similar results are found except that at low heat-pulse levels heat release is still very nearly exponential. Since off-center Na ions carry a dipole moment which has a random site, their pairwise interaction causes a random, near-static arrangement of the dipoles. In this arrangement, called the dipole glass state, the Na average displacement vanishes but not its rms value. The random displacements of Na in the glass state give rise to random fields at the Ta ion which depend on the particular site.

For this situation, scenarios have been devised in which a moment was allowed to flip if certain conditions regarding the surrounding moments were met.[15,16] One of these scenarios produced the famous Kohlrausch function for the decay of the total moment as given by Eq. (2). We also note that the short-term decay has been predicted to occur as $t^{-\beta}$ in an analytical analysis of spin glasses.[17]

We find a correlation between nonexponential decay of heat release and glass formation. Above the minimum[5] concentration required for the formation of a polar $x=0.12$ phase, relaxation is nonexponential. This coincides with independent information obtained on glass formation: Dielectric relaxation crosses over from exponential to arithmetic[5] and a logarithmic dependence of the sound velocity on T is observed[18] whenever $x > 0.12$. As in spin glasses, prolonged treatment of the sample with the conjugate field enhances relaxation times and nonexponentiality. The reason is that clusters of correlated orientations may form during treatment. The relation $\ln\tau = \exp(N_c/4)$ accounts for the obvious fact that clusters composed of a large number N_c of constituents relax more slowly than small clusters do.[19] Accordingly, application of transient fields, increasing the holding time, and increasing the heat pulse, all tend to accommodate quadrupoles over larger correlation lengths. Our results give conclusive evidence that regular lattice sites and not only impurity sites exhibit Kohlrausch relaxation. This is the first direct observation of its kind and indicates that random-site dipoles couple strongly to the lattice,[20] quite in contrast to random-site spins in spin glasses.[19]

We have thus been able to interpret heat-release data for the first time in terms of an energy-level diagram based on the nuclear quadrupole of ^{181}Ta. This new method allowed us to determine the properties of nuclear quadrupoles in ordered and disordered systems. We find that quadrupoles relax exponentially in an ordered crystal, whereas their relaxation function is given instead by the stretched-exponential Kohlrausch function when disorder is introduced by Na doping. Relaxation is prolonged and made more nonexponential by an increase of the doping level and of the heat input and by prolonged holding times. The metastability associated with such relaxation is considered to be a consequence of the hierarchical structure of relaxation paths as they were first found in spin glasses.

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