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Order-disorder mixed phase in TlH_2PO_4

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An intermediate phase of partial order, associated with antiferroelectricity, is elucidated in hydrogen-bonded TlH_2PO_4 undergoing separated antiferroelectric and ferroelastic phase transitions. Our ^1H and ^{31}P nuclear magnetic resonance linewidth measurements revealed marked changes at an intermediate phase boundary, involving an intermediate phase of mixed order of coexistence of paraelectricity and antiferroelectricity, which was identified by means of impedance spectroscopy. A coupling of the proton and the PO_4 tetrahedral motions to the proton ordering in the hydrogen bonds is also manifested.

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The KH_2PO_4 (KDP)-type crystals mostly undergo a ferroelectric transition, and only a few of them undergo an antiferroelectric transition. Thus, the hydrogen-bonded antiferroelectrics are much less understood.[1] The antiferroelectric transition in the hydrogen-bonded antiferroelectrics has been reported to be associated with the lattice strain, and some ferroelectrics under external pressure exhibited antiferroelectric phases.[2] The ferroelectric and ferroelastic phase transitions are well known to be of a weak first order in the hydrogen-bonded KDP-type crystals.[3–6] The electric and elastic properties associated with the transitions have been investigated in terms of the domain wall motions.[7,8] Observation of coexisting order-disorder and displacive behavior in these ferroelectrics is considered to be a breakthrough in the field.[9–11]

TlH_2PO_4 (TDP) and TlH_2AsO_4 are known to have two distinct domain structures, one being the (001)/(100) domain structure, which disappears above the ferroelastic phase, and the other being the (201) domain structure, which persists above T_c'.[12] The interface regions between the two domains can have some random stress-strain relationships, leading to elastic frustrations in the ferroelastic phase.[13] While the ferroelectric and ferroelastic transitions occur simultaneously in KDP, the antiferroelectric and ferroelastic phase transitions in TDP, with a heavy ion and short hydrogen bonds of three distinct types, occur at different temperatures, i.e., at $T_c=230$ K and at $T_c'=357$ K, respectively.[14–16] In the ferroelastic phase of TDP where the antiferroelectric transition takes place, the strain-polarization coupling, which is responsible for a sharp anomaly of the dielectric constant at T_c', is readily expected to dominate the dielectric properties.[17,18]

The dielectric constant measurements alone, which has usually been the case, are not sufficient to study the ferroelastic transition in the KDP-type systems.[19,20] Some ac impedance measurements have been carried out, but only to investigate the high temperature anomaly of the KDP family, which arises from the thermal decomposition near the surface.[21,22] In this work, the ferroelastic phase in TDP was investigated by means of impedance spectroscopy and nuclear magnetic resonance (NMR). Thus, a peculiar phase boundary is identified from the temperature-dependent impedance spectroscopy data, and an apparent coupling between the polarization and the microscopic lattice dynamics associated with protons in the hydrogen bonds as well as the PO_4 tetrahedra undergoing reorientation motions is revealed.

A TDP polycrystalline pellet as well as a *b*-cut single crystal were used for the measurements in the temperature range of 280–400 K. The complex impedance was measured using a Quadtech 7600 impedance analyzer in the frequency range between 10 Hz and 2 MHz. The experimental impedance data were analyzed in terms of the equivalent circuit models. A Bruker MSL 200 spectrometer was used for the ^1H NMR measurements. The line shapes were obtained by Fourier transforming the free-induction decay signals. The high-resolution ^{31}P magic angle spinning NMR measurements for TDP were made at the Larmor frequency of 243 MHz at the spinning frequency of 7 kHz. The chemical shift was measured relative to a ^{31}P standard, 85% aqueous solution of H_3PO_4.

In our recent impedance spectroscopy study in TDP,[23] distinct electrical responses were identified by an equivalent circuit analysis of a polycrystalline sample in distinct temperature ranges, separated by a Curie-Weiss temperature $T_s=327$ K obtained from the extrapolation of the dielectric susceptibility in the paraelectric phase, well above the antiferroelectric phase transition temperature $T_c=230$ K. Under dc bias voltages applied in the (010) direction for a *b*-cut TDP single crystal, a paraelectric response of the polarization was observed above $T_s=327$ K, whereas an antiferroelectric response was observed below T_s.[23,25]

The dc bias dependencies of the capacitive components in the polycrystalline sample were measured both below and above T_s, as shown in Fig. 1. A characteristic dc bias dependence with the capacitance monotonically decreasing with increasing dc bias is noticed above T_s, indicative of a paraelectric response. On the other hand, below T_s, the two distinct capacitances obtained from the equivalent circuit analysis display quite distinct dc bias dependencies, one being a paraelectric response and the other being an antiferroelectric response.[25] In other words, an increase of dielectric constant [C_1 in Fig. 1(a)] by the application of a dc electric field[25] is a signature of antiferroelectricity. Thus, T_s, in fact, can be taken to be a phase boundary separating two distinct phases, and the temperature range between the macroscopic antiferroelectric phase transition temperature and the phase

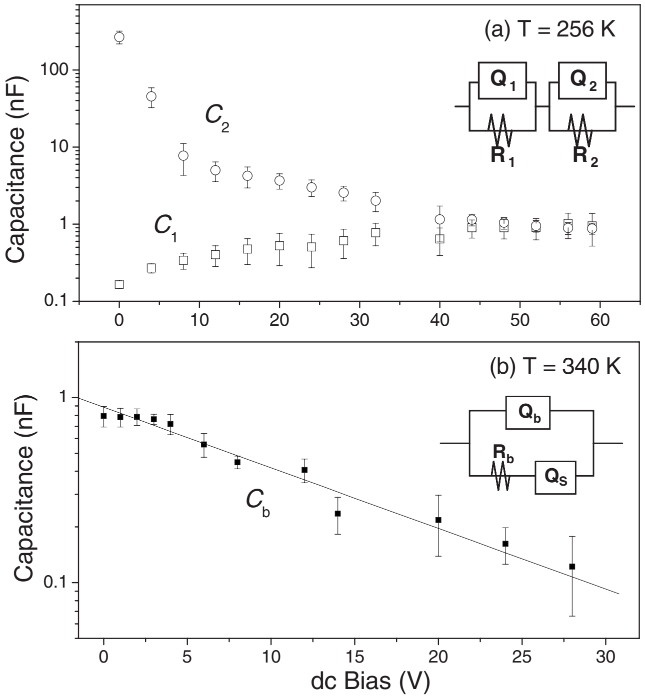

FIG. 1. (a) Capacitance-voltage (C-V) characteristics, obtained from the equivalent circuit models, for a TDP polycrystalline sample at T=256 K and (b) at T=340 K above the mixed-phase boundary T_s=327 K. Below T_s, the equivalent circuit model consists of two RC circuits, whereas above T_s, where the Cole-Cole plot displays a low-frequency tail, the subscripts b and s indicate the high-frequency and low-frequency regions, representing the bulk and the surface regions, respectively (Refs. 23 and 24).

boundary temperature T_s can, indeed, be identified as a paraelectric-antiferroelectric mixed phase.

In order to further elucidate the nature of the temperature T_s representing distinct electrical responses, microscopic lattice dynamics in the TDP system was studied by means of ^{1}H and ^{31}P NMR probing the proton and the PO$_4$ tetrahedral motions, respectively. The proton motion in the O-H···O hydrogen bonds can be reflected in the ^{1}H NMR line shape in TDP, consisting of a broad Gaussian line component and a narrow Lorentzian one (inset of Fig. 2). The Gaussian line arises from the "rigid lattice" protons, whereas the Lorentzian line arises from the mobile protons undergoing hopping motions, fast in the time scale probed by the NMR Larmor frequency. In Fig. 2 showing the temperature dependence of the Gaussian linewidth representing the rigid lattice, motional narrowing takes place at T_s=327 K. In view of the possible coupling of the polarization and the proton motions, it is quite interesting that the "mixed-phase boundary" identified from the electrical responses turns out also to mark changes in the microscopic proton dynamics.

It is interesting to note the temperature dependence of the high-resolution ^{31}P NMR linewidth in Fig. 3, where the antiferroelectric phase transition is sensitively reflected. The linewidth shows little change above the antiferroelectric phase transition temperature T_c before abruptly displaying motional narrowing at T_s. The temperature dependence in Fig. 3 above T_c is quite similar to that in Fig. 2, in very good agreement with the proton-lattice coupling model,[4,26,27] whereby the H$_2$PO$_4$ tetrahedral reorientational motion and the proton configurational motion around a given phosphate take place synchronously (Slater-Takagi defects).

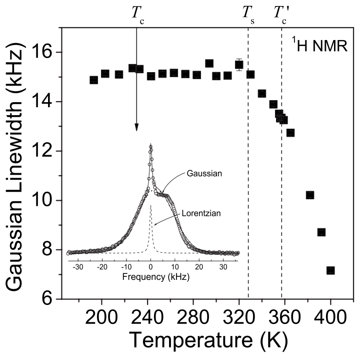

FIG. 2. Temperature dependence of the Gaussian linewidth in TDP. Inset: ^{1}H NMR line shape at 270 K. The open circles correspond to the data points, and the dashed lines correspond to the Gaussian and Lorentzian line components.

The observed temperature independence of the ^{1}H and ^{31}P NMR linewidths between T_c and T_s deserves special attention. The mixed H-bonded types in the TDP crystal with coexisting antiferroelectric and paraelectric orders may be taken to bear a similarity to a frustrated magnetic spin system. While both single phases of antiferroelectricity ($T<T_c$) and paraelectricity ($T>T_s$) show motional narrowing of the homogeneous NMR linewidth with increasing temperature, the mixed phase ($T_c<T<T_s$) exhibits temperature independence associated with the contribution of the inhomogeneous NMR linewidth.[28] The dipole moments have, in fact, been theoretically explained to be closely connected with the proton configurations around the PO$_4$ groups.[29] Thus, the lattice dynamics reflected in the proton and phosphorous NMR (Figs. 2 and 3) turns out to sensitively reflect the phase boundary of a paraelectric-antiferroelectric mixed phase identified by means of the impedance spectroscopy, which is associated with the order-disorder of the electric dipole moments in the TDP system.

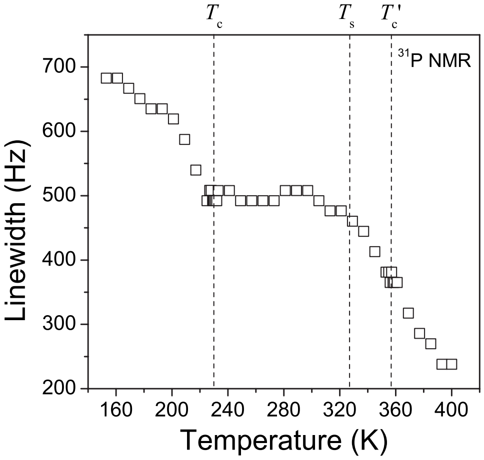

FIG. 3. Temperature dependence of the high-resolution ^{31}P NMR linewidth in TDP.

Our work also represents an important experimental revelation of the coupling between light and heavy ions in relation to the transitions in the system. In fact, recent *ab initio* calculations have theoretically shown the strong correlation between H and heavy ions and its implication in the phase transition of the KDP system.[30,31] In this regard, our work is a strong experimental verification of this fact performed in a member of the KDP family.

In summary, a peculiar intermediate phase of mixed order, involving coexistence of paraelectricity and antiferroelectricity, has been identified in the ferroelastic phase of hydrogen-bonded TlH_2PO_4 by means of impedance spectroscopy measurements. Furthermore, ^1H and ^{31}P nuclear magnetic resonance measurements revealed a coupling of the order in the electric moments to the dynamics of protons in the hydrogen bonds and the PO_4 tetrahedra undergoing reorientational motions.

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