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LETTER TO THE EDITOR

High-precision ^{31}P chemical shift measurements on KH$_2$PO$_4$-type crystals: role of electronic instability in the ferroelectric transition mechanism

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Abstract
The mechanism of the ferroelectric transition in KH$_2$PO$_4$-type crystals has been probed using magic angle spinning ^{31}P NMR on single crystals. The higher resolution thus obtained has enabled us to detect a marked change in the ^{31}P isotropic chemical shift around the transition temperature T_c, with a clear jump at T_c. These results are interpreted as evidence that the transition involves a displacive component with electronic instabilities playing a role in the driving mechanism.

The atomic-level details of the ferroelectric phase transitions in KH$_2$PO$_4$ (KDP) and its analogues still remain unclear, despite several decades of studies. One important unresolved issue is whether the transition is driven by a pure order/disorder process involving the ordering of the hydrogens (Hs) along the O–H . . . O bond, or whether electronic instabilities are simultaneously involved in the transition mechanism [1, 2]. It appears that the theoretical process has been hampered by the lack of experimental techniques [1] that can clearly distinguish between the order–disorder versus displacive mechanisms [1]. In this regard it was suggested some time ago [1, 3] that accurate measurements of the temperature dependence of the isotropic part of the NMR chemical shift, σ_{iso}, through the phase transition temperature, T_c, could provide an answer. This is based on the fact that σ_{iso}, being a trace of the chemical shift tensor, is invariant to any pure translational or rotational change of a given molecular moiety. Thus a clear detection of an anomaly in the σ_{iso} around T_c would imply the involvement of electronic instabilities (and thus a displacive component) in the transition mechanism, whereas the lack of an anomaly would point to a pure order/disorder behaviour. In fact, KD$_2$PO$_4$ (DKDP) was the first investigated from this view, and since no change in ^{31}P σ_{iso} was measurable at T_c (223 K), it was concluded that the transition mechanism must be of the pure order/disorder type. Similar conclusions have been subsequently derived for the transition of CsD$_2$PO$_4$ [4]. Since these conclusions are of high significance in the further developments of theoretical models, we have reexamined the earlier data. On chemical grounds it was concluded that, since the anticipated change in σ_{iso} at T_c is small—about 100 Hz (a few parts
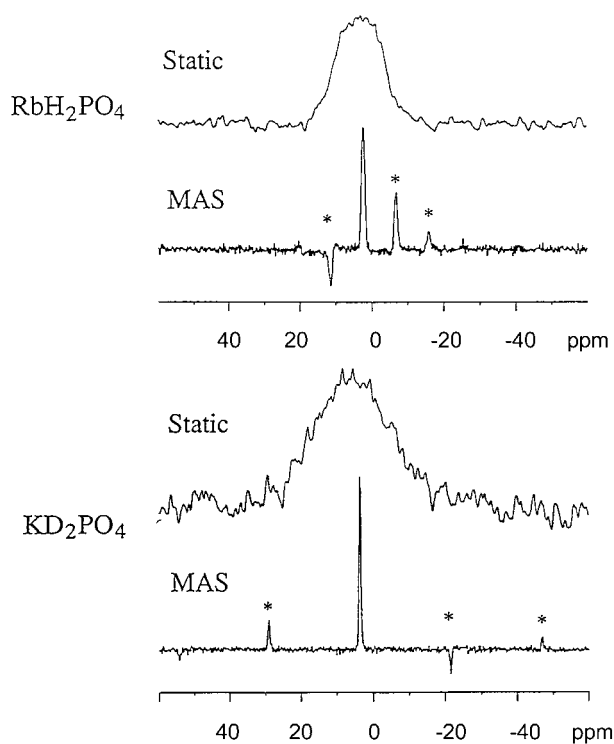
per million at most)—it could be well hidden in the NMR signal linewidths, which are in the range of 20–30 kHz [1, 3]. On the other hand it is known that the recently developed high resolution techniques for solids, involving magic angle spinning (MAS) [5], especially with the utilization of single crystals [6, 7], can lead to orders of magnitude narrower NMR peaks from solids. In this letter, we report high-precision NMR measurements of the ^{31}P nucleus in the PO_4 moieties in several members of the KDP family, including KD_2PO_4, and find that there is a clear and pronounced change in the measured σ_{iso} around the T_cs of the investigated materials. These results point to a significant role played by electronic instabilities in the mechanism of the phase transition, and have led to a theoretical model that provides a consistent explanation for both the observed order/disorder and displacive features of the phase transition in these materials.

In the MAS technique, a powder sample is spun around an axis that makes an angle of 54, 7° degrees (the magic angle) with the direction of the Zeeman field. MAS narrows the NMR linewidths in solids by averaging the anisotropic components of the chemical shift tensor, as well as the magnetic dipole–dipole couplings, both of which vary as $(3\cos^2\Theta - 1)$. Thus at $\Theta = 54.7°$ degrees, both of the anisotropies are averaged out if the spinning speed is greater than the magnitudes of the anisotropies involved. Simultaneously a strong rf pulse is applied at the resonance frequencies of the isotropically j-coupled nuclei. In addition, the utilization of single crystals instead of powders has been shown to lead to a further, up to a factor of five, enhancement in resolution, as was demonstrated recently for ^{13}C nuclei in the organic crystal squaric acid [5], because single crystals exhibit no line broadening effects due to anisotropic bulk magnetic susceptibility. Here we used the MAS method with single crystals. The measurements were performed with a standard Bruker spectrometer operating at 300 and 600 MHz (protons), with a temperature control of 0.01 K, essentially as described earlier for the ^{13}C studies [5, 6].

Figure 1 shows a comparison of the ^{31}P NMR signals from single crystals of 90% deuter-ated $KD_{1.8}H_{0.2}PO_4$ ($D_{1.8}KDP$) and RbH_2PO_4 (RDP), at room temperature. The two upper spectra depict the signal from a static single crystal, essentially as reported earlier [2], whereas the corresponding two bottom spectra show the signals under MAS, with the same crystals spinning at 7 kHz. The linewidth is about 20 kHz for the non-spinning case, and only about 70 Hz under MAS, thus clearly demonstrating the order of magnitude higher spectral resolution obtained with the presently reported method. This also enabled us to detect the change in the peak position around T_c. Here σ_{iso} is measured relative to the spectrometer frequency setting for a ^{31}P standard, a solution of H_3PO_4. As is customary, the shifts to low fields are refereed to as positive, which yields an overall diamagnetic susceptibility (i.e. negative).

In order to check the above results, we carried out similar measurements on fully deuterated (99.9%) crystals of DKDP as obtained from Aldrich Chemical Co., and recrystallized from D_2O under nitrogen. Little or no change in σ_{iso} was observed for these samples. It is known that such extremely highly deuterated DKDP loses its ferroelectric properties. The lack of a phase transition in these crystals was additionally verified via specific heat measurements from 77 to 300 K in our laboratory.

Figures 2 and 3 show the temperature dependence of the chemical shift for $D_{1.8}KDP$ and RDP. Clearly, σ_{iso} varies significantly with temperature in the paraelectric phase and shows a clear break at the T_c of 202 K for $D_{1.8}KDP$ and 147 K for RDP. The shift exhibits a distinct discontinuity at T_c while the linewidth shows an abrupt increase below T_c, in agreement with the (near) first order nature of the phase transition, and an anticipated pronounced distortion in the PO_4 moiety. The linewidth change will not be analysed here, since it seems to be at least partly due to a lack of the needed faster spinning speed to average out the increased anisotropy in the chemical shift below T_c.

Static

RbH$_2$PO$_4$

MAS

* * *

40   20   0   -20   -40   ppm

Static

KD$_2$PO$_4$

MAS

*   *   *

40   20   0   -20   -40   ppm

Figure 1. Comparison of NMR spectra for RDP (upper panel) and D$_{1.8}$KDP (lower panel) between static (upper spectra) and MAS (bottom spectrum) methods. * indicates MAS spinning sidebands.
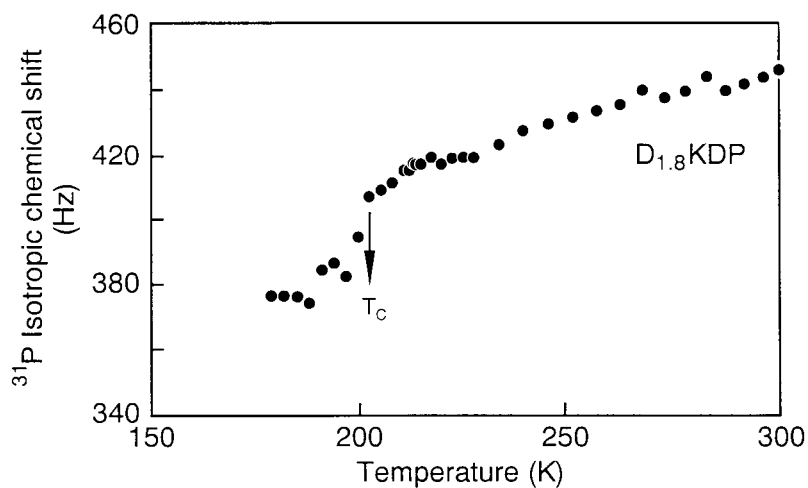
Figure 2. ^{31}P isotropic chemical shift of D$_{1.8}$KDP as function of temperature.

The observation of a temperature dependent component in the ^{31}P isotropic chemical shift σ_{iso} in the paraelectric phase points directly to a mechanism driving the phase transition, which involves charge transfer and electronic instability effects. This clearly means that a pure pseudospin approach [1] is inadequate in modelling the dynamics of KDP and its analogues.
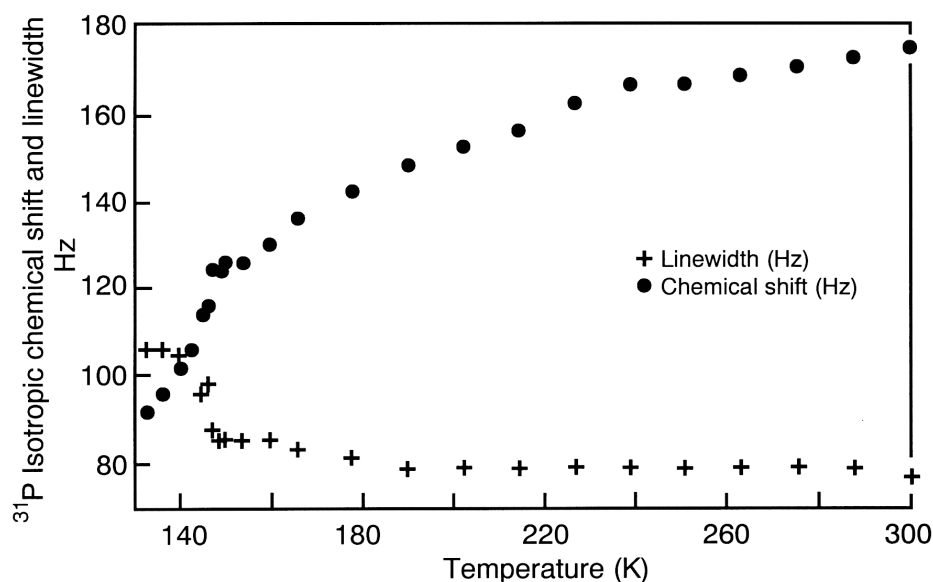
Figure 3. ^{31}P isotropic chemical shift and line width of RDP as function of temperature.

As has already been shown recently [7, 8] a consistent description of the phase transition and the large isotope effect on T_c in this class of crystals can be given if the exact O–H . . . O bond geometry is included and, most importantly, effects arising from the heavy ion sublattice are incorporated. Since it is well known that the PO_4 groups dominantly contribute to the dipole moment appearing below T_c, a major role of the driving mechanism in the phase transition is attributed to these units by modelling them within the nonlinear polarizability model which has been very successfully applied to perovskite type ferroelectrics ABO_3 [9]. Thus a close analogy is set up between the PO_4 units in KDP-type systems and the BO_3 units in ABO_3-type compounds, where the BO_3 are known to play the dominant role in the ferroelectric instability. The polarizability model goes beyond previous descriptions of the ferroelectric phase transition since here charge transfer and electron–phonon coupling effects are explicitly incorporated by using a nonlinear shell model [9, 10]. In order to account for the difference between perovskite type ferroelectrics and hydrogen bonded ones, the nonlinear dynamics of the phosphate groups are coupled to the hydrogens where it is assumed that their dynamics can be modelled by the pseudospin mechanism. It is important to emphasize here that the protons are treated nonadiabatically [10]. Also it has to be pointed out that the pseudospin Hamiltonian, used to describe the proton dynamics, contains a two-body interaction term $J(\vec{q})S^z(\vec{q})S^z(-\vec{q})$, where $J(\vec{q})$ has been shown to be a good approximation to the Slater–Takagi four-body forces [11]. Yet in contrast to previous approaches $J(\vec{q})$ in our model is substantially and temperature dependently modified through the coupling to the lattice. We thus consider a doubled nonlinear system where displacive features arise within the heavy ion units while order–disorder dyanmics are inherent to the protons [7, 8]. Taking into account that the two equilibrium positions of the protons along the y, z-axes between two PO_4 units are given by $(\delta_y/2, \delta_z/2)$ and $(-\delta_y/2, -\delta_z/2)$ with respect to the bond centre, it has been shown [8] that the coupling between the protons and the PO_4 units varies linearly with δ_z. This geometric arrangement of the hydrogen bonds with respect to the PO_4 units along the y, z-direction, which induces an asymmetry in the proton double-well potential, has been shown to be the

origin of the large isotope effect observed upon deuteration [8]. Since the largest principal component of the measured ^{31}P chemical shift tensor is parallel to the line connecting these O...H...O bonds, we have concentrated on temperature dependent dynamical geometrical changes in the proton potential which arise through the coupling to the nonlinear host lattice via the z-component in the proton potential.

In order to include the proton dynamics in the nonlinear shell model, the pseudospin tunnelling model is coupled to the electronic degrees of freedom of the nonlinear host lattice [8]. At T_c, both the tunnelling mode and the host lattice associated soft mode freeze out, thus inducing the spontaneous polarization. This process is accompanied by a small charge transfer from the oxygen atoms to the protons, which is equivalent to a covalent component in the O–H...O bond. In order to avoid lengthy details which are irrelevant for the following analysis we concentrate here on the proton–lattice-coupling term H_{TL} only and refer for further details to [7] and [8]. H_{TL} is modelled by two back to back Morse potentials V^M between the pseudospins S^z related to the protons and the shells (which are the equivalent of the oxygen related p electrons) of the neighboring PO$_4$ groups. The potential for each proton is then given by

$$V = \sum \frac{1}{2}(1 + \varepsilon_\pm S^z)[V^M(|\vec{X}_\pm(r)|) + V^M(|\vec{X}_\pm(l)|)] \tag{1}$$

with $\varepsilon_+ = +1, \varepsilon = -1$. The separation between the proton and the centre of the left (l) or right (r) PO$_4$ shell is

$$|\vec{X}_\pm(\xi)| = \{(R - R_0 \mp \varepsilon_\xi \delta_y/2)^2 + (u(\xi) \mp \delta_z/2)^2\}^{1/2} \tag{2}$$

where $\xi = r, l$ with $\varepsilon_\xi = +1, -1$ and $2R$ being the equilibrium distance between the neighboring PO$_4$ groups. $u(\xi)$ is the shell displacement coordinate along the z-axis. It is important to note here that the PO$_4$ core–shell coupling is nonlinear, which yields a T-dependent component on a mean field level. The Morse potential is given by

$$V^M(|\vec{X}|) = D[\exp(2 - \alpha|\vec{X}|) - 2\exp(-\alpha|\vec{X}|)] \tag{3}$$

where D, α, R_0 are parameters which are listed in table 1. Note that V^M is not a symmetric double-well potential. It becomes a symmetric one for $\delta_z = 0$ [12], where $\delta_y = \delta \cos \Psi, \delta_z = \delta \sin \Psi, \delta$ is the proton site splitting and Ψ the inclination angle between the y-axis and the proton hopping trajectory. Due to the coupling to the oxygen ion shells, this potential experiences an additional modification and adopts a temperature dependent component, which is treated on a mean-field level corresponding to performing the thermal average:

$$\langle u(\xi)^2 \rangle_T = \sum_{q,j} \frac{\hbar}{m\omega_{q,j}} \coth\left(\frac{\hbar\omega_{q,j}}{2l_B T}\right). \tag{4}$$

Here q, j refer to the momentum and phonon branch respectively. It is important to emphasize here that the coupling to the temperature dependent shell displacements is fully equivalent to temperature dependent charge fluctuations which, at T_c, freeze out thus inducing a charge transfer. It has been observed in perovskites, that a transition metal–oxygen charge transfer of less than 0.1 electron is sufficient to destabilize the lattice [13]. Similar small effects are expected in hydrogen-bonded systems and are believed to be the reason why earlier NMR experiments had resolution problems in observing these pecularities [1–4, 14]. Inserting equation (4) into equation (3), the temperature dependence of the Morse potential is obtained together with its dynamically induced asymmetry $\varphi(T)$, which is determined through the last term in equation (2). This introduces a relevant new concept in the treatment of hydrogen bonds, since the Morse potential is in general assumed to be independent of temperature. It is important to note here that the asymmetry of the local potential is exclusively due to the

coupling of the proton dynamics to the fluctuating oxygen ion shells. This implies immediately that the direct proton–proton interaction term $J(\vec{q})$ consists of at least two different terms which can be related to the Slater–Takagi energy parameters. In order to compare theoretical and experimental results directly, the measured data have had the value of σ_{iso} obtained at T_c subtracted and and been divided by a constant factor. The theoretical results on the other hand have been analysed in terms of the asymmetry of the potential, which reflects the dynamical probability distribution of the protons to stay for a longer period in a preferred well. The temperature dependent asymmetry $\varphi(T) - \varphi(T = T_c)$ is shown in figure 4 together with the experimental data. The good agreement substantiates the earlier conclusions [2] about a direct relation between the proton dynamics and the ^{31}P chemical shift tensor. We note, however, that there might be other explanations for the presently reported data. It has been pointed out, for example, that the observed temperature dependence for the ^{31}P chemical shift might be related to just the thermal effects on atomic positions. But from the investigation of a fully deuterated sample, that exhibits no phase transition, no temperature dependence in the chemical shift has been observed, which nearly excludes the possibility of thermal effects. Yet further work is thus still needed to fully understand the implications of the present results.

Table 1. Morse potential parameters used for RDP and $D_{1.8}$KDP.

	R [Å]	R_0 [Å]	α [Å^{-1}]	D [eV]
RDP	1.24	1.0918	4.68	2.94
$D_{1.8}$KDP	1.265	1.1119	4.68	2.94
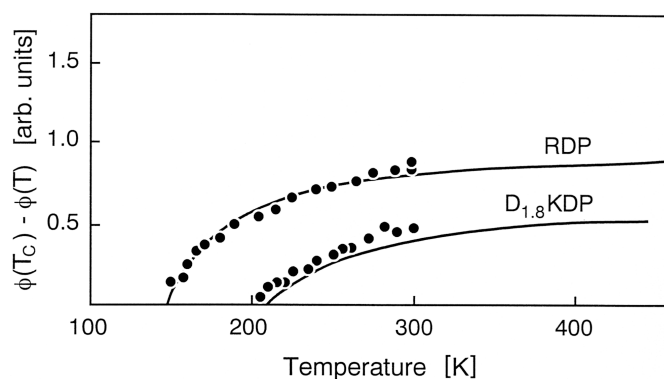
Figure 4. Temperature dependence of the normalized ^{31}P isotropic chemical shift σ_{iso} (for details see the text) (dots are experimental data points) and the calculated normalized Morse potential asymmetry $\varphi(T_c) - \varphi(T)$.

In conclusion, our new data together with their theoretical modelling suggest that the understanding of this interesting class of materials has to be extended to account for charge transfer and displacive effects. It was possible to detect these features essentially because of the very high resolution afforded by our NMR technique for ^{31}P. Similar measurements and theoretical analysis should be applicable to related systems, like the low-dimensional compound CsD_2PO_4 for which also previous studies failed to detect any change in the ^{31}P isotropic part around its T_c [3].

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