Dependence of the Dynamic Central Peak on Deuterium Content in Paraelectric KH_2PO_4

R. Blinc and J. Slak
J. Stefan Institute, University of Ljubljana, Ljubljana, Yugoslavia

and

F. C. Sa Barreto and A. S. T. Pires
Departamento de Fisica, Instituto de Ciencias Exatas, Universidade Federal de Minas Gerais, Belo Horizonte, Brazil

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Measurements of the temperature and frequency dependence of the proton and deuteron spin-lattice relaxation time T_1 show the presence of a dynamic central peak in paraelectric KH_2PO_4 which exhibits a dramatic narrowing on deuteration. The observed central-peak narrowing on deuteration qualitatively agrees with a continued-fraction calculation demonstrating that small dynamic intrinsic clusters may occur in KH_2PO_4-type crystals above T_c in addition to large static defect-induced clusters observed in light-scattering experiments.

The nature of the narrow central peaks (CP), which have been observed by electron paramagnetic resonance[1] (EPR), nuclear magnetic resonance[2,3] (NMR), dielectric relaxation,[4] and neutron,[5] light,[6] and Mössbauer-scattering[7] techniques to occur in addition to the soft mode in the order-parameter fluctuation spectra of systems approaching structural phase transitions from above, is still an open problem. Their occurrence cannot be understood within a linear-response theory in systems like paraelectric KH_2PO_4 (potassium dihydrogen phosphate, KDP) where the order fluctuations cannot directly couple to the temperature fluctuations, and explanations based either on "intrinsic" nonlinear cluster dynamics[8] or "extrinsic" impurity effects[9] have been proposed. The natural abundance (0.016%) of deuterium isotopes in H-bonded ferroelectrics has been suggested as a possible CP-inducing defect.[10] Though it seems clear that different experimental techniques see different central peaks, most of the observed CP have not yet been assigned to specific mechanisms or defects. The general opinion—based on the observation of static CP in light-scattering experiments—seems at present to favor the extrinsic theory of the origin of the CP.

We would like to point out that this opinion is not necessarily correct since light-scattering experiments are—in view of the proportionality of the Rayleigh-scattering cross section to the sixth power of the radius of the scattering center—selectively sensitive to large (and therefore static) defect-induced clusters, whereas they are blind to small (dynamic) intrinsic clusters. The NMR spin-lattice relaxation (T_1) technique, on the other hand, measures the spectral density of the fluctuations at the nuclear Larmor frequency and is thus selectively sensitive to the presence of dynamic fluctuating clusters, whereas it is completely blind to static clusters. The light-scattering and the NMR T_1 technique are thus complementary to each other and one should use the latter when searching for dynamic intrinsic clusters.

A clear-cut distinction between intrinsic and extrinsic CP in H-bonded ferroelectrics can be made on the basis of the isotope effect in the width of the CP. The intrinsic dynamic CP in deuterated systems should be narrower than in undeuterated systems by several orders of magnitude, whereas this is not the case for a dynamic impurity-induced extrinsic CP.

In this Letter we report the results of an NMR study of the frequency and temperature dependence of the proton and deuteron T_1 in paraelectric KDP and deuterated KDP, which we believe represents the first direct observation of the narrowing of a dynamic central peak on deuteration. The central peak in deuterated KDP is by more than two orders of magnitude narrower than the dynamic central peak in paraelectric KDP. We also present the results of a continued-fraction calculation of the order-parameter fluctuation spectrum of KDP as a function of deuterium content which indeed qualitatively reproduces the observed central-peak narrowing on deuteration. Both studies together represent strong evidence that small dynamic intrinsic clusters occur in KDP-type crystals in addition to large static defect-induced clusters observed in light-scattering experiments. Our study shows as well that naturally abundant deuterium cannot be the cause of the observed static (light-scattering)

and dynamic (T_1 NMR) central peaks in KH_2PO_4.

The experimental results are presented in Figs. 1 and 2. The temperature dependence of the proton T_1 in a rather pure KH_2PO_4 single crystal was measured at $\nu_I = 10.75$ MHz and of the deuteron T_1 in KD_2PO_4 at $\nu_L = 10.6$ MHz. The proton T_1 in KH_2PO_4 exhibits a pronounced peak at T_c [Fig. 1(a)] whereas the deuteron T_1 in KD_2PO_4 strongly decreases on approaching the transition temperature, $T_1 \to 0$ as $T \to T_c$ [Fig. 1(b)]. In both cases the T_1 results are not affected by the thermal history of the samples. The deuteron T_1 in KD_2PO_4 is at $T - T_c = 1$ K as well as at $T - T_c = -1$ K independent of the nuclear Larmor frequency in the range between 11 000 and 100 G [Fig. 2(a)], i.e., in the whole range over which measurements could be performed with our field-cycling spectrometer. The proton T_1 in KH_2PO_4, on the other hand, is strongly frequency dependent [Fig. 2(b)] and decreases with decreasing magnetic field.

The nuclear spin-lattice relaxation rate T_1^{-1} is proportional to the spectral density $j(\omega_L)$ of the order-parameter fluctuations—which modulate the proton magnetic dipole-dipole and deuteron quadrupole couplings—at the nuclear Larmor frequency ω_L. The above results thus show that the order-parameter fluctuation spectrum in KH_2PO_4 around 10.75 MHz is not flat, as expected for an overdamped soft mode, but increases in intensity at lower frequencies as expected for a spectrum exhibiting a central peak. The increase in T_1 on approaching T_c in KH_2PO_4 demonstrates that the width of the central peak becomes narrower than the proton-nuclear Larmor frequency so that $j(\omega_L)$ decreases as $T \to T_c$.

The deuteron T_1 results, on the other hand, demonstrate that the order-parameter fluctuation spectrum in KD_2PO_4 around 10.6 MHz is indeed flat and thus characteristic of an overdamped

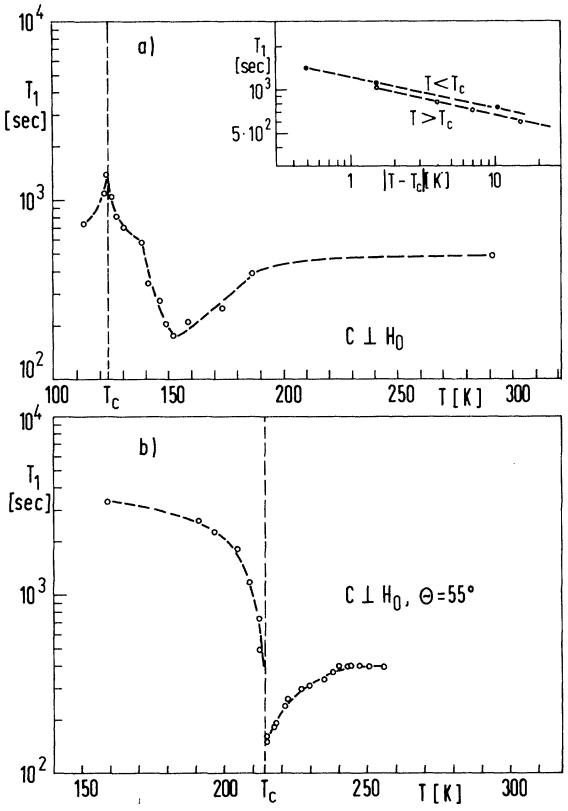

FIG. 1. Temperature dependence of (a) the proton spin-lattice relaxation time T_1 in a KH_2PO_4 single crystal at $\nu_L = 10.75$ MHz and (b) the deuteron spin-lattice relaxation time T_1 in a KD_2PO_4 single crystal at $\nu_L = 10.6$ MHz. The inset to (a) shows that the proton T_1 can be close to T_c in KH_2PO_4 described by a power law $T_1 \propto (T - T_c)^{\gamma - \Delta}$ with $\Delta - \gamma = 0.25$.

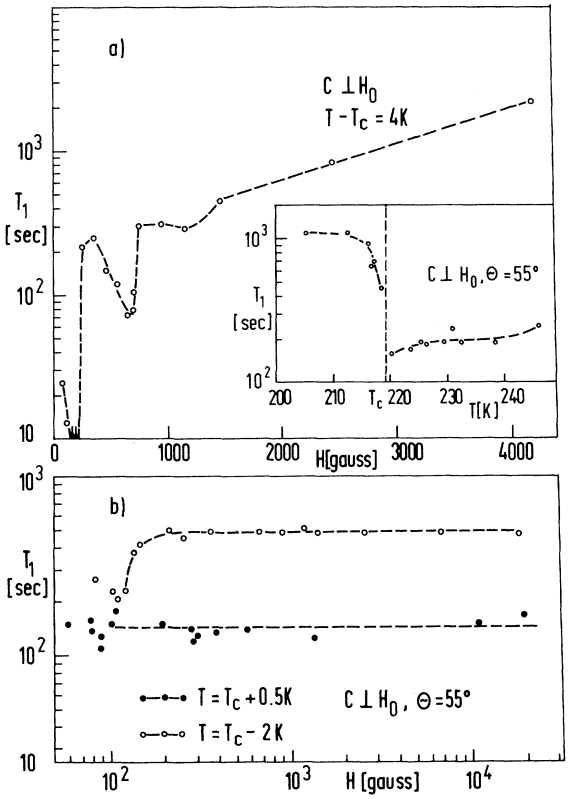

FIG. 2. (a) The proton spin-lattice relaxation time T_1 in a KH_2PO_4 single crystal and (b) the deuteron spin-lattice relaxation time T_1 in a KD_2PO_4 single crystal, as function of the external magnetic field H_0. The inset to (a) shows the temperature dependence of the deuteron T_1 at $H_0 = 100$ G.

soft mode. The decrease in the deuteron T_1 on approaching T_c reflects the increase in $j(\omega_L)$ due to the decrease in the soft-mode frequency. Using a magnetic-field cycling technique, we have repeated the measurements of the temperature dependence of the deuteron T_1 in KD_2PO_4 at $H_0 = 100$ G, i.e., at a Larmor frequency of 66 kHz. Again the same soft-mode behavior was found as at 10.6 MHz [see inset to Fig. 2(a)]. This demonstrates that the central peak in KD_2PO_4 is narrower than 66 kHz whereas it is of the order of 10 MHz in KH_2PO_4.

Using the wave-number–dependent dynamic susceptibility[9] which is normally used for a phenomenological description of systems exhibiting both a soft mode $[\omega_{q,\mathrm{crit}}^2 \propto (T - T_c)]$ and a central peak, as well as the fluctuation-dissipation theorem, one finds that close to T_c the deuteron T_1 results can be described by

$$T_1^{-1} \propto \epsilon^{-\gamma - \Delta + 3\nu}, \tag{1}$$

where $\epsilon = (T - T_c)/T$ and we assumed, in the spirit of dynamic scaling, that $\chi(0, q) \propto \epsilon^{-\gamma} f(q\xi)$, $\omega_q^2 \propto \epsilon^{\Delta} g(q\xi)$, and $\xi = \xi_0 \epsilon^{-\nu}$. Here γ, Δ, and ν are critical exponents and $f \approx g^{-1}$ will be functions of the product of the wave vector q and the correlation length ξ. In deriving expression (1) we assumed that ω_L is much smaller than the soft-mode frequency and much larger than the central-peak width, so that T_1^{-1} is dominated by soft-mode fluctuations.

If, however, the Larmor frequency is of the order of the central-peak width and $\omega_q < b$ (where b describes[9] the coupling between the soft-mode and the central-peak fluctuations), T_1^{-1} is dominated by central-peak fluctuations and we find that

$$T_1^{-1} \propto \epsilon^{\Delta - \gamma} / \omega_L^2. \tag{2}$$

In contrast to the former case, T_1 exhibits a peak at T_c if $\Delta > \gamma$ and is proportional to the square of the nuclear Larmor frequency. The proton T_1 data in KDP can be described by Eq. (2) with $\Delta - \gamma = 0.25$ [see inset to Fig. 1(a)].

The temperature and frequency dependences of the proton and deuteron spin-lattice relaxation rates thus show that the dynamic central peak in paraelectric KDP narrows on deuteration by more than two orders of magnitude. This behavior agrees with the results of a recent calculation[11] of the dependence of the intensity and width of the intrinsic central peak on the deuterium content[12] in H-bonded ferroelectrics using Mori's continued-fraction representation.[13]

The details of the calculation will be presented elsewhere. Here we would like to point out that in contrast to a "pure" system ($C_p = 1$ or $C_d = 1$), we have now *two* narrow central peaks and *two* broad overdamped soft modes.

The variation of the half-widths of the two central peaks with deuterium concentration is shown in Fig. 3(a). The deuteronlike central peak becomes narrower and the protonlike broader with increasing deuterium concentration.

The dependence of the intensities of the two central peaks at $\omega = 0$ on deuterium concentration is presented in Fig. 3(b). At $T = 1.01 T_c$ the deuteronlike central peak becomes stronger than the protonlike one only for a deuteron concentration C_d which is larger than 2.5%. For naturally abundant deuterium the deuteronlike central peak is weaker by four orders of magnitude than the protonlike one so that it—contrary to what has

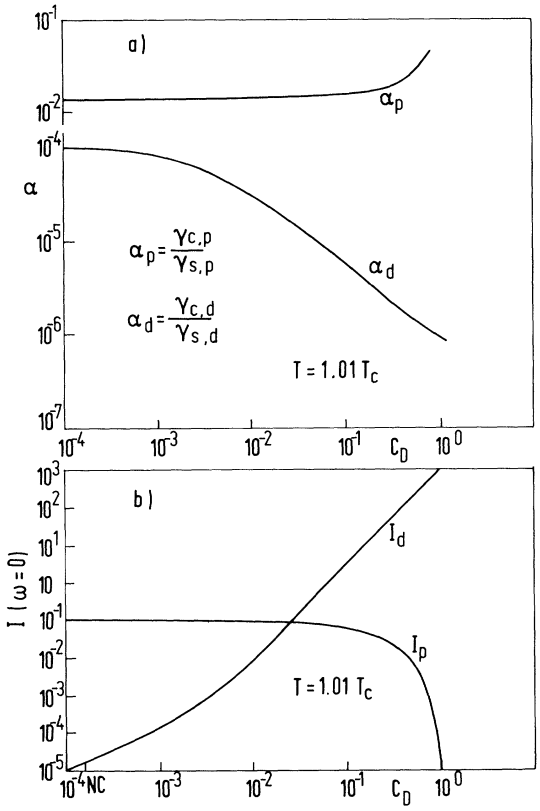

FIG. 3. (a) Dependence of the ratio α between the half-widths γ_c of the protonlike and deuteronlike central peaks and the corresponding soft-mode half-width γ_s on deuterium concentration. (b) Dependence of the intensity of the protonlike and deuteronlike central peaks at $\omega = 0$ on the deuterium concentrations. The following values (Ref. 11) for the parameters of the model Hamiltonian (Ref. 12) have been used: $J_{ij}^{pp} = J_{ij}^{dd} = J_{ij}^{pd} = 70$ cm^{-1}, $\Omega_H = 144$ cm^{-1}, and $\Omega_D = 1$ cm^{-1}.

been suggested—cannot account for the observed static central peak seen in KDP in light-scattering experiments.[6,10] The static central peak seen by light scattering in KDP[6] is thus almost certainly due to elastic strains and is not of intrinsic origin. The dynamic central peak observed in KDP by NMR spin-lattice relaxation measurements does, however, exhibit the predicted narrowing on deuteration and does not (as does the static one) depend on the thermal history of the sample. It thus seems feasible that the dynamic central peak seen in paraelectric KDP by NMR T_1 measurements is of intrinsic origin and due to small fluctuating clusters, i.e., islands of the low-temperature phase in the high-temperature phase. This is supported by the fact that the softening of the soft mode saturates close to T_c in KDP-type crystals[14] as well as in $SrTiO_3$[15] and that this phenomenon is sample independent. The stabilization of the soft-mode frequency by short-range ordered clusters above T_c is analogous to the stabilization by long-range order below T_c.

Small fluctuationg clusters also account for the dynamic central-peak effects seen in cw ^{75}As quadrupole perturbed NMR by Bjorkstam[2,3] and Adriaenssens[4] in paraelectric KH_2AsO_4. The lifetime effects in the EPR spectra of AsO_4^{3-}- and Cr^{5+}-doped KDP-type crystals[1] far above T_c may also be associated with small dynamic, clusters, though these clusters are probably trapped by the paramagnetic defect center and their dynamics is different from the one seen in NMR T_1 experiments in undoped crystals. Systematic studies on partially deuterated crystals may provide a definite answer to the question on the nature of the dynamic central peak in hydrogen-bonded ferroelectrics.

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