Disappearing Central Peak in Paraelectric Potassium Dihydrogen Phosphate (KDP)

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The quasielastic central peak of paraelectric potassium dihydrogen phosphate is suppressed by annealing. The solf-branch Brillouin spectra are then fitted with a classical coupled-mode expression without any deviation that could suggest additional contributions, and with parameters in good agreement with the available data.

Quasielastic central peaks (CP) observed at a number of phase transitions have been a matter of considerable interest.[1] The origin of those critical CP's occurring *in addition* to the expected soft mode (also when this soft mode is overdamped), and in cases where order-parameter fluctuations are not directly coupled to temperature fluctuations,[2] is a topic of current debate. Although intrinsic cluster mechanisms have been proposed to account for those features, it appears that observations made to data above the the transition temperature should rather be ascribed to impurities or other defects.[3] To my knowledge, however, there is not a single example where an observed CP coul yet be related to a specific defect. For this reason, a series of systematic Brillouin-scattering experiments was undertaken on KDP (potassium dihydrogen phosphate) as high-quality samples are easily obtained.[4] The main result presented here is that the previously reported quasielastic CP of KDP[5,6] can be strongly suppressed by annealing. Furthermore, a classical coupled-mode expression fits then *perfectly* (with statistical deviations only) the Brillouin spectra. This establishes that an observable dynamic CP contribution is also absent from those spectra.

In KDP, H tunneling couples to a polar optic mode whose softening produces the transition at the clamped Curie temperature T_C. Piezoelectric coupling to xy shear raises the Curie temperature to the free value T_a. The transition is slightly first order at ambient pressure and occurs at $T_{tr} > T_a$.[7] The soft branch is seen in the $x+z$, $(y, x+z)$, $x-z$ scattering geometry used here and for which a CP occurs as first reported by Lagakos and Cummins.[5] Recent observations indicate that near T_{tr} this CP is static.[6] It was suggested that the natural abundance of deuterium impurities (D) could possibly explain the CP-to-Brillouin-peak intensity ratio.[8] This assummed a freezeout[9] of D, a fact which remained to be checked experimentally.

Brillouin experiments with several crystals of

increased D content have now confirmed the spectra theoretically predicted.[10] However, instead of a vanishingly small single-particle relaxation frequency ν_D, one observes $\nu_D \simeq 4$ cm^{-1}, similar to that of fully deuterated KDP at a much more elevated temperature.[11] Hence, the D contribution to the spectra remains broad down to T_{tr} and no freezeout occurs. Furthermore, the size of the quasielastic CP observed in each case, did exhibit appreciable sample-to-sample variation without correlation to the D content. An attempt to correlate the CP strength with the Na concentration (another abundant impurity) was equally unsuccessful.

In search for a CP mechanism involving quenched defects, it appeared opportune to heat treat the material above room temperature. This was done with the $\frac{1}{2}$-in.-cubed crystals immersed in an inert fluid (pentadecane) and enclosed in a gold-plate copper container. A short (~ 10 min) treatment up to $\sim 100°C$ reduced the relative CP strength observed at the center of a crystal to less than one-third its original value. This suggests that this change is not associated with impurity diffusion towards the outside but rather with local cancellation of intrinsic defects, possibly dislocations. Prolonged annealing (18 h at 140°C) of a crystal with a small initial CP produced the sample for which results are reported here.[12] Its CP-to-Brillouin-peak intensity ratio near T_{tr} became ~ 0.02 as compared to the value ~ 1 commonly found in fresh samples. Photographic observation of the depolarized scattered beam from this crystal revealed a uniform light column at $T_{tr} + 0.3$ K. Very near T_{tr} a weak structure of slightly lighter static spots is evident. Although a quantitative measurement of the relative intensity of such poorly defined speckles would be difficult, it appears reasonable that they might carry about 2% of the scattered intensity. In this case, the left-over CP could still be attributed to the same mechanism that produced the original one.[7] Annealing at much higher temperatures is unfortunately prevented by a

destructive transition occurring near 175°C.[13] The fact that the KDP CP is annealable recalls the result of Yagi, Tanaka, and Tatsuzaki on $KH_3(SeO_3)_2$.[14]

The Brillouin spectrometer consisted of a single-mode Ar-ion laser operating on the 4880-Å line, a single-pass piezoelectrically scanned planar Fabry-Perot interferometer of 0.487^3 cm^{-1} free-spectral range, a photocounting system followed by a multichannel analyzer, and a device coupler for on-line transfer to an APL (A Programming Language) time-sharing system. The present spectra were accumulated in 200 scans of 5 sec each, triggered by the laser line. Several orders of raw data were folded into 51 channels covering one-half of the free-spectral range. This was then fitted with the theoretical line shape as explained below. The sample temperature could be read with $\frac{1}{3}$ mK precision and kept to 1 mK over the duration of a measurement. Local heating by the laser beam (~ 0.2 mK/mW) was seen on the spectra so that the laser power was kept below 10 mW. The scattered light was collected with a 30-mrad acceptance and no spectral modification was apparent upon reduction of this angle.

The observed spectrum is the convolution of $I(\omega) = \mathcal{Q}\, \mathcal{R}(\omega) + \mathcal{B} + \mathcal{C}\, \delta(\omega)$ with the instrumental response. $\mathcal{R}(\omega)$ is the normalized spectral response function $S(q,\omega)$, $\mathcal{B}$ is the background of dark counts, and $\mathcal{C}$ is the remaining CP intensity. $S(q,\omega)$ is given by a standard coupled-mode expression[6,11]

$$S(q,\omega) = \frac{kT}{\pi\omega}\operatorname{Im}\left[(a\ p) \begin{pmatrix} \chi_p^{-1} & -g \\ -g & \chi_a^{-1} \end{pmatrix}^{-1} \begin{pmatrix} a \\ p \end{pmatrix} \right] \qquad (1)$$

with $\chi_p(\omega) = 1/A\,(\omega_c^2 - i\gamma\omega - \omega^2)$ for the soft ferroelectric mode and $\chi_a(q,\omega) = \omega_a^2/C(\omega_a^2 - i\gamma_a\omega - \omega^2)$ for the bare acoustic mode. Here, a, p, g, and C are the appropriate electro-optic, piezo-optic, piezoelectric, and bare elastic constants, respectively. In mean-field approximation (MFA), ω_c^2 is proportional to $T - T_c$. The acoustic frequency is given by $\omega_a^2 = q^2C/\rho_M$, with ρ_M the mass density; in the present experiment $\omega_a = 0.256$ cm^{-1} near T_{tr}.

In order to appreciate the information that can be derived from the spectra, and the number of parameters involved in the fits, it is necessary to discuss Eq. (1) in some detail. It is known from Raman-scattering results[5] that in the accessible temperature region $(T > T_{tr})$ $\omega_c > 10$ cm^{-1} and $\gamma > 100$ cm^{-1}. It follows that at the frequencies of present interest $(\omega \lesssim \omega_a)$ the ω^2 term is negligible in χ_p. Hence, the Brillouin spectra can only determine the products $A\omega_c^2$ and $A\gamma$, or equivalently the ratios $Q \equiv \omega_c^2/\bar{\omega}^2$ and $\tau \equiv \gamma/\bar{\omega}^2$, where the piezoelectric coupling strength $\bar{\omega}^2 \equiv g^2/AC$ equals ω_c^2 at $T = T_a$. Furthermore, the bare-phonon damping being experimentally very small, one can set $\gamma_a = 0$ in χ_a. Then the spectral shape $\mathcal{R}(\omega)$ depends on ω_a^2, on Q and τ, and on one further dimensionless parameter $\alpha \equiv aC/gp$. The latter is fairly well known from available data, and was determined experimentally from a relative measurement of the Brillouin intensity over a large temperature interval.[10] Near T_{tr} we find $\alpha = 6.5$. Given ω_a^2 (and to a lesser extent α), it should be noted that Q and τ are always well determined by the spectra. Indeed one finds that (1) is somewhat similar to a simple harmonic response $\propto [(\Omega_{Br}^2 - \omega^2)^2 + \Gamma_{Br}^2\omega^2]^{-1}$, where $\Omega_{Br}^2 = \omega_a^2(Q-1)/Q$ and $\Gamma_{Br} = \tau\omega_a^2/Q^2$, and it happens that $2\Omega_B > \Gamma_{Br}$ (underdamped response) in the accessible temperature range $(T > T_{tr})$.

Figure 1(a) shows the experimental values of Q-1 plotted versus $T - T_a$, where T_a is obtained
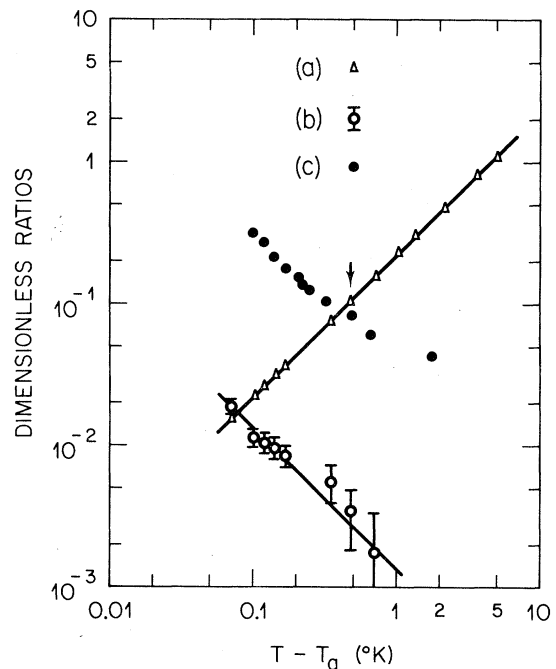

FIG. 1. (a) The reduced soft-mode frequency $\omega_c^2/\bar{\omega}^2 - 1$ and (b) the CP–to–Brillouin-peak intensity ratio plotted vs $T - T_a$ for the annealed crystal. (c) The CP–to–Brillouin-peak intensity ratio before annealing vs $T - T_a$. The value of T_a previous to annealing was determined from the reduced soft-mode frequency by a plot similar to (a).

from the extrapolation of $Q - 1$ to zero. In MFA, and neglecting the temperature dependence of $\bar{\omega}^2$, one has $Q - 1 = (T - T_a)/(T_a - T_c)$. The straight line gives $T_a = 121.703$ K and $T_a - T_c = 4.537$ K. The inverse of the total scattered intensity extrapolates to zero at T_a within the present accuracy. The random error on $T_a - T_c$ is fairly small (± 0.003 K), but the value is somewhat sensitive to the precise choice of α which is a possible explanation for the slight discrepancy with the ultrasonic result $T_a - T_c = 4.37$ K.[15] One also finds T_{tr} 121.76 K, which indicates that the first-order nature of the transition ($T_{tr} - T_a \simeq 60$ mK) is not appreciably modified by annealing. All thirteen spectra were fitted with $\tau = 0.84$ cm, and a noticeable deterioration of the fits occurs for τ departing by ± 0.02 cm from that value. To compare this with Raman results one advantageously considers the ratio $Q/\tau = \omega_c^2/\gamma \equiv B(T - T_C)$, as the slope B is fairly well determined by that data. The present value is $B = 0.262$ cm^{-1} K^{-1} whereas one obtains $B = 0.295$ cm^{-1} K^{-1} from Ref. 5, and $B = 0.277$ cm^{-1} K^{-1} from She et al.,[16] so that all values are in reasonable agreement.

The most important point of these fits is that they are statistically perfect. The deviations did not show any systematic trend and the χ^2 was close to 1 for each spectrum, as illustrated in Fig. 2. In fact, the mean of χ^2 for all thirteen spectra was 0.83 and its standard deviation 0.25. The last figure compares well with the theoretical standard deviation 0.21 of a χ^2 distribution with $51 - 5 = 46$ degrees of freedom. Furthermore, as the total number of photocounts in one spectrum was $\sim 3 \times 10^4$ for the highest T and over 10^6 for the lowest T, one can state conservatively that the difference between theoretical and experimental spectra, if any, is smaller than
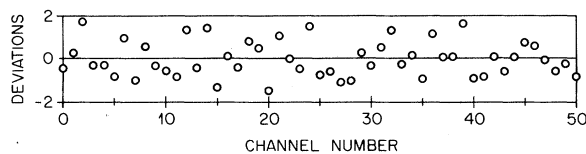

FIG. 2. A *typical* deviation plot. This plot applies to the experimental point indicated by the arrow in Fig. 1. For this spectrum the integrated number of photocurrents is 2×10^5. The abscissa covers one-half freespectral range, with the laser frequency at channel 0, and the Brillouin peak around channel 13 with 1.2×10^4 counts. The ordinate at channel i is $\sigma_i = (n_i - n_i)/\sqrt{n_i}$ is the measured and N_i the calculated photocurrent numbers. The χ^2 is $\sum \sigma_i^2/46 = 0.69$ for this particular fit.

1% at high T and 0.1% at low T. Hence, an observable dynamic CP is absent from the Brillouin spectra. It should be emphasized that this conclusion does not exclude the possiblity of a broad CP contribution to the ferroelectric-mode spectra.[17]

Given the high quality of the fits, reliable values are extracted for the CP to Brillouin-peak intensity ratios $(e - e_0)/\alpha$, where e_0 is the high-temperature limit of e. Figures 1(b) and 1(c) present the ratios observed after and before annealing, respectively. e_0 is almost equal to e for the highest-temperature points in Fig. 1(b), producing large error bars. The $(T - T_a)^{-1}$ dependence indicated by the straight line is in keeping with MFA treatments of the CP.[18] Previous to annealing, such a simple linear dependence is apparently not obeyed.[19] Both the identification of the active defects in fresh crystals and our theoretical understanding are, as yet, insufficient to advance an explanation for this behavior.

In summary, the static CP of KDP is suppressed by suitable annealing and presumably can be eliminated in structurally perfect crystals. The dynamics of the acoustic soft mode obeys classical theory remarkably well, in agreement with recent considerations on the upper marginal dimensionality in this type of system.[20] The removal of the disturbing CP feature opens the way to reliable experiments, in particular lightscattering ones, on critical and multicritical phenomena in this important model substance. Conversely, the theoretical and experimental study of critical phenomena in structurally imperfect systems appears to be a worthwhile endeavor.

[1]See, e.g., *Proceedings of the International Conference on Lattice Dynamics*, edited by M. Balkanski (Flammarion Sciences, Paris, 1977), pp. 731–754.

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[4]The growth of KDP has been much perfected due to its electro-optic applications. The samples were purchased from Cleveland Crystals Inc., Cleveland, Ohio 44117.

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[10]Detailed results will be published elsewhere.

[11]R. L. Reese, I. J. Fritz, and H. Z. Cummins, Phys. Rev. B 7, 4165 (1973).

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[19]Note that dead-time corrections on count rates have been made, and have never been very large.

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Stochastic Theory of Bimolecular, Heterogeneous, Surface Catalytic Reactions

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A stochastic theory of heterogeneous bimolecular reactions catalyzed by active sites is formulated using a defect-renormalized propagator method. Reaction between adsorbed migrating species occurs upon their coincidence on active sites and may demand proper internal-state configurations. Effects due to spatial heterogeneity, lattice structure, and internal states on the reaction evolution are analyzed.

We present a stochastic theory of bimolecular reactions catalyzed by a surface, which follow a *generalized Langmuir-Hinshelwood mechanism*,[1,2] where adsorbed reactants *migrate* on the surface and reaction occurs only upon their coincidence on *active sites*.[3] Additionally, the particles may possess *internal states* (energetic, spin configuration, or orientational) and the reaction cross section may depend on the internal states of the reacting species. Mechanisms involving reactant surface diffusion to active sites have been invoked recently in the analysis of several catalytic systems of interest: For example, based on statistical thermodynamics considerations it has been concluded that the disproportionation reaction of ethylene on a supported rhenium oxide catalyst[4] (and similarly[5a] for propylene on WO_3) proceeds via surface migration and subsequent

reaction on specific surface sites ("site-localized diffusion"[5b]); molecular beam data of H_2/D_2 exchange on stepped Pt(111) surfaces have been interpreted in terms of adatom surface migration to surface steps where reaction occurs[6]; surface migration was found to be the rate-limiting step in a number of high-temperature reactions—the oxidation of polycrystalline Mo,[7] the decomposition of formic acid[8] above 455°K, the halogenation of Si and Ge surfaces,[8] and the oxidation of the basal plane of graphite.[9] In order to achieve a comprehensive understanding of catalytic systems of the type considered in this study, such as to allow an optimization of system parameters for maximum yield, it is necessary to construct a microscopic theory which goes beyond the traditional "mass action law" approaches. Our formulation and the derived expressions for the mean

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