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Deuterium Impurities and the Rayleigh Central Peak in Hydrogen-Bonded Ferroelectrics

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Results of a mean-field treatment of deuterium impurities in hydrogen-bonded ferroelectrics are compared with observations of the critical central peak in potassium dihydrogen phosphate. The natural abundance of deuterium accounts quantiatively for the relative strength and temperature dependence of the peak. Its slow dynamics and the absence of a similar feature in cesium dihydrogen arsenate are commented on.

The occurrence of a critical central peak (CP) in addition to the normal soft mode in the spectra of materials approaching phase transitions from above has stirred considerable interest. Explanations based either on intrinsic nonlinear cluster dynamics or on impurity effects have been proposed.[1] Halperin and Varma have recently shown within the mean-field approximation (MFA) that a small concentration of defects more susceptible than the host is in principle able to account for observations near displacive transitions.[2] They replaced the isolated defects by a uniform distribution over all lattice sites (effective-crystal approximation or ECA) and postulated the defect

dynamics. Moreover, Höck and Thomas have pointed out that the local dynamics of single defects can be considerably modified on the approach of the host transition at T_{tr}.[3] Under favorable conditions, impurities can even "freeze out" (acquire a nonzero local order parameter) at a temperature $T_f > T_{tr}$. This effect, obtained in MFA, results from a cooperation of all modes in the soft branch and is not contained in the ECA. If we relax the MFA, a real freeze-out cannot be expected, but a qualitative change in impurity dynamics is likely to occur around T_f. This appears confirmed by recent observations on Cr^{5+} intentionally substituted for As^{5+} in potassium dihydrogen arsenate (KDA).[4] In the present Letter, deuterium (D) impurities, always present in hydrogen-bonded ferroelectrics, are considered quantitatively. The treatment accounts, with no adjustable parameter, for the relative strength of the CP and Brillouin peaks (BP) observed to-date in potassium dihydrogen phosphate (KDP).[5,6] It is the first time that the strength of a CP is explained quantitatively.

It is well known that proton tunneling plays an important role in KDP isomorphs and can be described by a pseudospin model.[7] The tunneling integral of deuterons is considerably smaller than that of protons. In KDP, the former can be taken equal to zero,[8] and the latter is $\Omega = 86.2$ cm^{-1}.[9] The proton motion is almost perpendicular to the ferroelectric z axis but strongly couples to a polar optic mode that produces the polarization P.[10] This results in a phase transition at the clamped Curie temperature T_C. In the paraelectric phase, the piezoelectric tensor component $g_{36} \equiv g$ couples P to the acoustic modes. The resulting softening of the xy shear branches raises the transition to the free Curie temperature T_a (a for acoustic). For KDP, I take $T_C \cong 117.8$°K and $T_a \cong 122.1$°K.[5,9] In effect, the transition at 1 bar is slightly first order and occurs at a temperature $T_{tr} > T_a$. In the notation and with the values of Schmidt, Western, and Baker,[11] $T_{tr} - T_a = 6B^2/25AC = (0.043 \pm 0.007)$°K for KDP which is of the same order as previous estimates[5] and will be used presently. The Hamiltonian of the coupled tunneling and optic modes is written as usual[12] except for two modifications: (i) Distinct pseudospin to optic-mode coupling constants, F_p and F_d for protons and deuterons, respectively, are used; (ii) a direct coupling of protons to the field E along z is neglected, which does not affect the final result significantly. Proceeding to the MFA and to a configurational average that amounts to the ECA, we find that the pseudospin system decomposes into two coupled subsystems, one for protons with the spin variable $\vec{p}$ and one for deuterons with the single spin component d_z.[12] The long-wavelength behavior is governed by the MFA Hamiltonians $\mathcal{H} = -\vec{p} \cdot \vec{H}_p$ and $\mathcal{H}_d = -d_z H_{dz}$, with

$$\vec{H}_p = (2\Omega, 0, J^{pp}(1-c)\langle p_z\rangle + J^{pd}c\langle d_z\rangle + F_p\langle Q\rangle), \tag{1a}$$

$$H_{dz} = J^{pd}(1-c)\langle p_z\rangle + J^{dd}c\langle d_z\rangle + F_d\langle Q\rangle. \tag{1b}$$

The notation is that of Ref. 12. The optical-phonon coordinate $\langle Q\rangle$ can be adiabatically eliminated from both the statics and the dynamics as the frequencies of interest in Rayleigh-Brillouin measurements are much below the optic-mode frequency ω_{op}. The phonon equation of motion reduces to

$$\omega_{op}^2\langle Q\rangle = (1-c)F_p\langle p_z\rangle + cF_d\langle d_z\rangle + \rho E. \tag{2}$$

After elimination of $\langle Q\rangle$ in (1) the interaction terms J^{mn} $(m, n = p, d)$ are replaced by effective interactions $\mathcal{J}^{mn} = J^{mn} + F_m F_n/\omega_{op}^2$, and the pseudospins couple to E.

In the paraelectric phase, only p_x has a nonvanishing thermodynamic expectation value $\langle p_x\rangle = \frac{1}{2}\tanh\beta\Omega$ where $\beta = 1/kT$. Transition to the ferroelectric state occurs when the self-consistency equations become compatible with $\langle p_z\rangle \neq 0$ and $\langle d_z\rangle \neq 0$, which for $c \ll 1$ leads to

$$\frac{d\ln T_c}{dc} = \frac{1}{\alpha\beta_0\Omega}\left[\frac{1}{4}\beta_0\frac{(\mathcal{J}^{pd})^2}{\mathcal{J}^{pp}} - 1\right], \tag{3}$$

with $\alpha \equiv (\mathcal{J}^{pp}/4\Omega) - (4\Omega/\mathcal{J}^{pp})$. β_0 corresponds to the transition temperature with $c = 0$ or

$$\beta_0 = \Omega^{-1}\operatorname{arctanh} 4\Omega/\mathcal{J}^{pp}. \tag{4}$$

The proton dynamics obeys a Bloch equation in accordance with $\mathcal{H}_p$. Phenomenological relaxation is added, with $T_2 \equiv \Gamma^{-1}$ describing transverse relaxation towards the instantaneous equilibrium direction of $\vec{p}$. Deuterons have a pure relaxation dynamics as given by $\mathcal{H}_d$ with a characteristic time $\tau \equiv \nu^{-1}$ which for the moment is assumed greater than 10^{-9} sec for KDP. Coupled linearized equations connecting p_y, p_z, and d_z are obtained. From these, the susceptibility $\chi_p(\omega)$ is calculated using $P = \mathfrak{N}\rho Q = \chi_p E$, where $\mathfrak{N}$ is the density of polarizable units. The determinant of the linear system is expanded to first order in $t \equiv \beta_c - \beta$ (with $\Omega t \ll 1$) and c (with $c \ll 1$). With only the leading term in the numerator and neglecting the noncritical pure-lattice part, one

finds

$$\chi_p(\omega) = \frac{\chi_0(\Gamma^2+4\Omega^2)}{\omega_\infty^2 - i\gamma\omega - \omega^2 - \delta^2/(1-i\omega\tau)}. \quad (5)$$

Here $\chi_0 = (\mathcal{K}/\mathcal{J}^{pp})(\rho F_p/\omega_{op}^2)^2$ and $\omega_\infty^2 = \omega_0^2 + \delta^2$ with

$$\omega_0^2 = \Omega\alpha t(\Gamma^2+4\Omega^2), \quad (6a)$$

$$\delta^2 = c\beta(\mathcal{J}^{pd})^2(\Gamma^2+4\Omega^2)/4\mathcal{J}^{pp}. \quad (6b)$$

$\gamma = \Gamma$ to zeroth order in c and t. Note that (5) has the familiar form that leads to a CP.[13] Finally, coupling of χ_p to the acoustic modes via g, and calculation of the scattering intensity can be made very simply.[14] In the $x+z$, $(y,x+z)$, $x-z$ scattering geometry used for observation of the acoustic soft mode,[5,6] the bare acoustic response is $\chi_a = q^2/\rho_M(\omega_a^2 - i\gamma_a\omega - \omega^2)$ with $\omega_a^2 = q^2C_{66}/\rho_M$ where q is the wave vector, C_{66} the bare elastic constant, and ρ_M the mass density. With the electro-optic and piezo-optic tensor components $a \equiv a_{36}$ and $p \equiv p_{66}$, respectively, the spectrum is proportional to[14]

$$S(q,\omega) = \frac{kT}{\pi\omega}\mathrm{Im}\left[(a\ \ p)\begin{pmatrix}\chi_p^{-1} & -g\\ -g & \chi_a^{-1}\end{pmatrix}^{-1}\begin{pmatrix}a\\ p\end{pmatrix}\right]. \quad (7)$$

The free Curie temperature T_a obtains when the susceptibility matrix in (7) has a pole at $\omega = 0$. This occurs for $\omega_0^2 = \chi_0(\Gamma^2+4\Omega^2)g^2/C_{66} \equiv \bar{\omega}^2$. The corresponding value of t in (6a) is defined as t_a. For KDP, $\Omega t_a \ll 1$, and the expansions leading to (5) and (6) remain valid around t_a. The final results are written in terms of $\bar{\omega}_0^2 = \omega_0^2 - \bar{\omega}^2$ and $\bar{\omega}_\infty^2 = \bar{\omega}_0^2 + \delta^2$. The former quantity is given by (6a) with t replaced by $t-t_a$. At low frequencies ($\omega^2, \gamma_a\omega \ll \omega_a^2$, and $\gamma\omega \ll \bar{\omega}_\infty^2$), one finds that (7) contains a CP,

$$S_C = \kappa\tau\delta^2/\pi(\bar{\omega}_0^4 + \omega^2\tau^2\bar{\omega}_\infty^4), \quad (8)$$

with $\kappa = kT(a+pg/C_{66})^2/\chi_0(\Gamma^2+4\Omega^2)$. This CP integrates to $\int_{-\infty}^{\infty} S_C d\omega = \kappa\delta^2/\bar{\omega}_0^2\bar{\omega}_\infty^2$. On the other hand, (7) obeys the sum rule $\int_{-\infty}^{\infty} S d\omega = (kTp^2/C_{66}) + \kappa/\bar{\omega}_0^2$. The first term is small and noncritical, and is neglected. The critical BP area is the total critical area minus that of the CP, or $\int_{-\infty}^{\infty} S_B d\omega = \kappa/\bar{\omega}_\infty^2$. Hence, the ratio of CP to BP intensities is $\delta^2/\bar{\omega}_0^2 \equiv x^{-1}$, where

$$x = \{4\Omega\alpha\mathcal{J}^{pp}/[cT_a(\mathcal{J}^{pd})^2]\}(T-T_a). \quad (9)$$

The CP intensity is proportional to $1/(x+x^2)$.

To compare with experiments, it remains to evaluate x. The natural abundance of D in KDP is the product of the distribution coefficient[15] times the natural abundance in water $c = 0.68 \times 1.5 \times 10^{-4} = 1.02 \times 10^{-4}$. $\mathcal{J}^{pp}$ is calculated from Ω and β_0 using (4). One finds $\mathcal{J}^{pp} = 432\ \mathrm{cm}^{-1}$, and $\alpha = 0.455$. $\mathcal{J}^{pd}$ is then obtained from Eq. (3) using $dT_a/dc = 107^\circ\mathrm{K} \cong dT_C/dc$.[15] The last equality applies as $T_a - T_C$ is relatively small and almost the same for $c = 0$ and $c = 1$.[14] One obtains $\mathcal{J}^{pd} = 445\ \mathrm{cm}^{-1}$. Using these values in (9), one obtains $x = 27.5(T-T_a)$. The observed Rayleigh intensities consist of the critical CP plus a background of noncritical entropy fluctuations and defect scattering. As the CP intensity decreases with $(T-T_a)^2$ at high T, the background is given by the highest-temperature point both in Refs. 5 and 6. After background subtraction, Ref. 5 gives the three CP to BP intensity ratios shown in Fig. 1. The abscissas are $T - T_{tr} = 0.13$, 0.23, and 0.52°K, with $T_{tr} - T_a$ as explained above. Error bars represent the estimated accuracy of the planimetry which is lowest for the highest-temperature point, because of the relative importance of background subtraction. There is no adjustable parameter in the comparison to x^{-1}. In Fig. 2, the predicted CP temperature dependence is compared to the experiment of Ref. 6. The background has been subtracted from the plotted points. The lowest-temperature point is at $T - T_{tr} = 0.03$°K. The intensity scale is the single adjustable parameter of this comparison. Though the extreme quality of the agreement might be somewhat fortuitous, it is remarkable that two independent experiments performed on different samples can be so well explained simultaneously. It suggests that D is the cause of the CP in KDP.

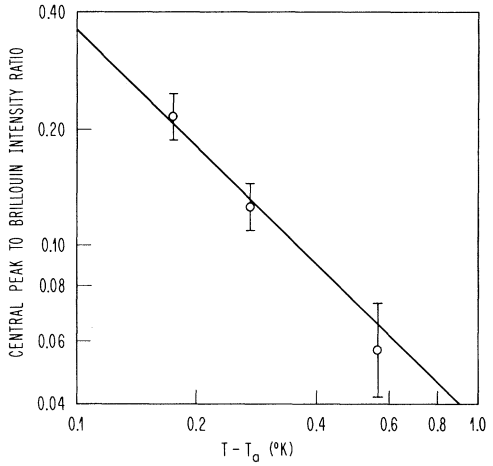

FIG. 1. Data points from Ref. 5, Fig. 2. The straight line is x^{-1} from the text.

For this to be the case, the D dynamics must become extremely slow, especially in view of Ref. 6. This suggests a freeze-out following the

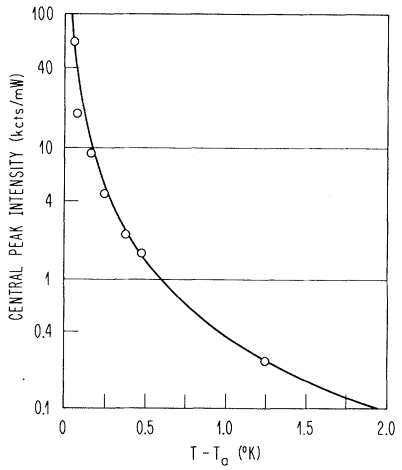

FIG. 2. Data points from Ref. 6. The solid line is a constant times $(x+x^2)^{-1}$.

mechanism proposed by Höck and Thomas.[3] If we neglect piezoelectric coupling, and assume that $\mathcal{J}_{ij}^{pd}$ and $\mathcal{J}_{ij}^{pp}$ are proportional for all lattice sites i, j, the D freeze-out condition is $\int[M\mathcal{J}_q^{pd} + MNJ_q^{pd}(\mathcal{J}_q^{pd}-\mathcal{J}_q^{pp})-1]/(1-N\mathcal{J}_q^{pp})d^3q = 0$. Here $\mathcal{J}_q$ is the Fourier transform of $\mathcal{J}_{ij}$, $M \equiv \beta/4$, $N \equiv (\tanh\beta\Omega)/4\Omega$, and the integration is over the entire Brillouin zone. Freeze-out occurs when the equality is satisfied with $\beta = 1/kT_f$, $T_f > T_{tr}$. For instance, with $\mathcal{J}_q^{pp} = \mathcal{J}^{pp}(1-q_z^2/q^2)$, one obtains $T_f = 140°K$. However, one expects additional dispersion in $\mathcal{J}_q^{pp}$,[16] which tends to reduce T_f. Piezoelectric coupling does increase T_f slightly, as will be explained elsewhere.[17] In order to draw firm conclusions, it is necessary to have exact values of $\mathcal{J}_q$, and these are not presently available for KDP.[18] This points to the need of additional experiments to establish D freeze-out.

The absence of similar CP in cesium dihydrogen arsenate[19] can have several explanations: (i) The transition is more first order than in KDP ($T_{tr} - T_a \simeq 1°K$)[19] so that an appreciable part of the critical increase is inaccessible; (ii) the distribution coefficient of D is smaller than in KDP (of the order of 0.28 at small c, as estimated by Loiacono *et al.*[20] (iii) the piezoelectric coupling is exceptionally large[19] and might push T_{tr} above T_f in which case the CP would presumably be too broad to be observed easily.

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