Evidence of macroscopically entangled protons in a mixed isotope crystal of KH$_p$D$_{1-p}$CO$_3$

François Fillaux$^{1,4}$, Alain Cousson$^2$ and Matthias J Gutmann$^3$

$^1$ LADIR-CNRS, UMR 7075, Université Pierre et Marie Curie, 2 rue Henry Dunant, F-94320 Thiais, France
$^2$ Laboratoire Léon Brillouin (CEA-CNRS), C E Saclay, F-91191 Gif-sur-Yvette Cedex, France
$^3$ ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK

E-mail: fillaux@glvt-cnrs.fr

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Abstract

We examine whether protons and deuterons in a crystal of KH$_{0.76}$D$_{0.24}$CO$_3$ at 300 K are particles or matter waves. The neutron scattering function measured over a broad range of reciprocal space reveals the enhanced diffraction pattern anticipated for antisymmetrized macroscopic states for protons (fermions). These features exclude a statistical distribution of protons and deuterons. Raman spectra are consistent with a mixture of KHCO$_3$ and KDCO$_3$ sublattices whose isomorphous structures are independent of the isotope content. We propose a theoretical framework for decoherence-free proton and deuteron states.

1. Introduction

A defect-free crystal is a macroscopic quantum system with spatial periodicity. In principle, only nonlocal observables are probed by plane waves, e.g. with diffraction or spectroscopy techniques. This is attested to by the marked localization in reciprocal space of Bragg peaks as well as discrete phonon states. However, since the seminal work of Slater [1], the nonlocal nature of protons is commonly overlooked in crystals containing bistable O–H···O hydrogen bonds, when the coexistence of two configurations, say ‘L’ for O1–H···O2 and ‘R’ for O1···H–O2, is conceived of as classical disorder. This leads to a conflict of interpretation in that a statistical distribution of protons should destroy the translation periodicity of the crystal, whereas infrared and Raman spectra show extended states at the Brillouin-zone center (BZC) obeying the symmetry-related selection rules of the crystal. This conflict has been tolerated because the nonlocal nature of protons cannot be shown by x-ray diffraction. Even with neutrons, a Bragg peak analysis is not conclusive, as statics and dynamics cannot be unraveled effectively from the unit cell structure factor [2].

The same conflict of interpretation arises for crystals containing hydrogen-bonded centrosymmetric dimers, such as carboxylic acids [3, 4] or potassium hydrogen carbonate (or bicarbonate, KHCO$_3$) [5–8]. The thermal interconversion between tautomeric configurations, LL and RR, is supposed to be correlated with a reorganization of the single and double CO bonds, along a reaction path across a multidimensional potential. This is commonly rationalized with rigid proton pairs in an asymmetric double well coupled to an incoherent thermal bath mimicking a liquid-like environment. It is supposed that ‘phonon-induced incoherent tunneling’ should prevail at low temperatures, whereas stochastic jumps should take the lead at elevated temperatures. In contrast, vibrational spectra are consistent with nonlocal observables represented by normal coordinates. There is no evidence of any symmetry breaking due to local disorder and the density of states remains discrete at any temperature [9–11].

Nowadays, the local or nonlocal behavior of bistable hydrogen bonds can be distinguished at advanced pulsed neutron sources, with a time-of-flight Laue diffractometer measuring a much broader range of reciprocal space than any reactor-based four-circle instrument. The scattering function measured at large momentum transfer values ($Q = k_f - k_i$, where $k_i$ and $k_f$ are the initial and final wavevectors, respectively).
features for the isomorphous derivative KDCO₃. To the best
planes. In contrast, there is no evidence of similar enhanced
cigar-like-shaped along Q vectors perpendicular to dimer
planes. In contrast, there is no evidence of similar enhanced features for the isomorphous derivative KDCO₃. To the best of our knowledge, the dramatic increase of both coherent and incoherent scattering intensities for the sublattice of protons, not observed for deuterons, cannot be explained by any conventional model based upon Slater’s localized particles. Alternatively, a quantum theory leads to different macroscopic quantum correlations (entanglement) for indistinguishable protons (fermions) or deuterons (bosons). The enhanced features can thus be explained by the spin symmetry of the ‘super-rigid’ fermion states for which phonons are forbidden. In contrast, deuteron states are represented by phonons with no spin symmetry.

Above 150 K, the less favored sites along the hydrogen bonds (R), at Δr ≈ 0.6 Å from the L sites, are progressively populated, while the space group symmetry and the unit cell parameters remain unchanged. At 300 K, the population ratio is ≈18(RR):82(LL). The enhanced features observed continuously from cryogenic to room temperature show that the quantum correlations are temperature-independent. The coexistence of LL and RR configurations is consistent with a quantum superposition of proton states perfectly insulated from decoherence by the other degrees of freedom [13, 14]. Then, scattering functions, vibrational spectra and quasi-elastic neutron scattering (QENS) data can be reinterpreted consistently with nonlocal observables and quantum interference arising from the superposition of macroscopic tunneling states.

Structural transitions of second order (P2₁/a ↔ C2/m) occur at Tc_H ≈ 318 K (KHCO₃) or Tc_D ≈ 353 K (KDCO₃). Above Tc, dimers split into two centrosymmetric entities, symmetric with respect to the plane (a, c). It is quite remarkable that the enhanced features of the scattering function, as well as proton dynamics and quantum interference, do not show any discontinuity at Tc [14]. There is no evidence of classical disorder above Tc. It transpires that quantum correlations arise from the space periodicity of centrosymmetric dimers, irrespective of the space group symmetry. Here, we examine whether the enhanced features survive, or not, in a mixed isotope crystal of KH₆D₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆₋₇₋₆
Figure 2. Diffraction patterns of KH\textsubscript{0.76}D\textsubscript{0.24}CO\textsubscript{3} at 300 K in (a\textsuperscript{*}, c\textsuperscript{*}) planes. The arrows point to the ridges of intensity for momentum transfer parallel to (z) and perpendicular to the trace of dimer planes (dashed lines), which contain the (x) direction, as defined in figure 1. The (y) direction parallel to (b\textsuperscript{*}) is perpendicular to (a\textsuperscript{*}, c\textsuperscript{*}) planes. \( k = Q_y/b^\ast \).

There was no evidence of any significant decrease of Bragg peak intensities into Laue monotonic diffuse scattering due to a statistical distribution of isotopes. Alternatively, for a sublattice of paired-up nonseparable protons and deuterons, the averaged scattering length should be

\[
\bar{b} = 0.76\bar{b}_\text{H} + 0.24\bar{b}_\text{D} \approx -1.242 \text{ fm}.
\]  

(2)

The model is more artificial because \( p \) is no longer a free parameter and it is less satisfactory (\( R \approx 4\% \)). However, it cannot be definitely excluded. Consequently, the question as to whether the sublattices of protons and deuterons are separable entities remains largely open.

The conclusions of the present work are based upon the neutron scattering function of the mixed isotope crystal presented in section 2. The enhanced features show that the quantum correlations of the pure crystal are not destroyed by partial deuteration and Raman spectra are consistent with separable proton and deuteron states. In section 3, the quantum theory \[14, 15\] applied to the mixed crystal accounts for macroscopic proton and deuteron states, each of which being a superposition of \( LL \) and \( RR \) states. A detailed interpretation of the enhanced features is proposed. In section 4, we show that alternative explanations are inappropriate.

2. Experimental details

2.1. The neutron scattering function

The mixed isotope crystal (\( \approx 30 \text{ mm}^3 \)) measured in the previous diffraction work \[16\] was cut from a twinning free parent crystal (\( \approx 20 \times 15 \times 3 \text{ mm}^3 \)) obtained from a water solution (\( \approx 75\% \text{H}_2\text{O}, 25\% \text{D}_2\text{O} \)). This parent crystal was loaded in the vacuum chamber of the time-of-flight Laue diffractometer SXD at the ISIS pulsed neutron source \[18, 19\]. The temperature was (300 ± 1) K. We measured eight orientations, each for \( \approx 8 \text{ h} \), with (b) parallel to the equatorial plane of the detector bank. The reduced data were concatenated in order to compute the scattering function (figure 2). Previous studies of crystals with similar sizes...
have shown that multiple scattering effects are not important. However, Bragg peaks show severe extinction. A standard analysis is consistent with the structure and isotope contents previously determined, but the modest precision (R ≈ 10%) shows that measurements conducted at different sources are complementary.

The interpretation of the scattering function is based upon the crystal structure made of centrosymmetric dimers lying in (103) planes with O⋯O bonds parallel to each other. Proton/deuteron coordinates are x, y, z, (figure 1), Qx, Qy, Qz, are projections of Q, and Uxx, Uyy, Uzz are the dominant temperature factors. Dotted lines in figure 1 enhance the network of double lines of proton/deuteron sites, either parallel to (b), separated by Δs ≈ 0.6 Å or parallel to x, with Δs ≈ 2.2 Å. The spatial periodicity of these grating-like structures is Ds ≈ a/cos 42° ≈ 20.39 Å or Ds = b. The distance between (x, y) planes is Ds ≈ 3.28 Å. A previous analysis of rigid-body motions has shown that there is no short-range correlation between protons and carbonate entities [12] and inelastic neutron scattering (INS) spectra show that proton dynamics are separated from heavy atoms and are virtually dispersion-free [20, 21].

In figure 2, cuts of the scattering function parallel to (a*, c*) show spots of intensity, corresponding to Bragg peaks, and, at large Q values, enhanced streaks along Qz perpendicular to the trace of dimer planes parallel to (Qx, Qy), with Qz ∥ (b*). These streaks are not an artifact of the instrument because: (i) the detectors were calibrated with vanadium; (ii) the streaks are measured by different detectors for each of the eight orientations of the crystal and (iii) spurious signals eventually due to an anomalous detector should appear along different trajectories.

The maps in figure 2 are similar to those of KHCO3 at the same temperature [13], apart from the weaker intensity of diffuse scattering due to the smaller concentration of protons. On the other hand, they are markedly different from those of KDCO3 for which enhanced features are totally extinguished [12]. The enhanced diffraction peaks correspond to nodes of the reciprocal sublattice of protons/deuterons and there is no obvious alternative sublattice with similar parameters. They occur when k = Qs/b* = ±2πn/a*(b*Δs) ≈ ±n,y × 2.57. For k = 0, in-phase scattering by double lines of sites parallel to x gives peaks at Qx = ±2π/Δs ≈ ±10.00 ± 0.25 Å⁻¹ and Qz ≈ nx × 1.92 Å⁻¹. At k = ±3, Δs ≈ 1, anti-phase scattering along Qy and Qz give peaks at Qy = ±(5.00 ± 0.25) Å⁻¹ and Qz ≈ nx × 1.92 Å⁻¹. For k = ±5 (n,y = 2) and k = ±8 (n,y = 3), the patterns of enhanced peaks are similar to those at k = 0 and k = ±3, respectively.

A cut along the streak at Qx = (10.00 ± 0.25) Å⁻¹ in the plane k = 0 (figure 3) shows enhanced Bragg peaks on the top of a continuum along Qz. Because there is no evidence of disorder along z, this continuum is essentially due to incoherent scattering [12]. It compares favorably with the Gaussian profile I0 exp(−Qs2Uzz/2), with Uzz ≈ 0.04 Å² [16]. Compared to the intensity I0 at Qs = 0, Qz = 0, the ratio I0/I10 ≈ 2, with substantial uncertainty, is much greater than expected from conventional models according to which incoherent scattering by protons should be proportional to the Debye–Waller factor for protons determined by neutron diffraction in [16].

The interpretation of the scattering function is based

![Figure 3](image-url)

**Figure 3.** Cut of the scattering function along Qz in the plane k = 0, at Qs = (10 ± 0.25) Å⁻¹, after background correction. The Gaussian profile exp(−Qs2Uzz/2), with a² = 0.04 Å² is representative of the Debye–Waller factor for protons determined by neutron diffraction in [16].

2.2. Separation of proton and deuteron states: Raman scattering

In figure 5, the Raman profile of the stretching mode νOD for the pure crystal is redshifted by ≈600 cm⁻¹ with respect to the νOH profile of KHCO3 and the spectrum of the isotope mixture is a mere superposition of these profiles. There is no visible frequency shift for each profile and, therefore, there is no significant dynamical correlation between isotopes.
In contrast, if protons and deuterons were paired up, a single $v_O(H_2D_2)$ profile should appear at an intermediate frequency, shifting smoothly from $v_O(p = 1)$ to $v_D(p = 0)$. This is clearly excluded. The spectra accord with separable proton and deuteron extended states consistent with the mixture of sublattices (1).

In addition, the $O \cdots O$ bond lengths are significantly different for KHCO$_3$ ($R_H = 2.58$ Å) or KDCO$_3$ ($R_D = 2.61$ Å) and $R_{0.76} = 2.59$ Å for KH$_{0.76}$D$_{0.24}$CO$_3$ is seemingly a weighted average [16]. Isomorphous sublattices of protons and deuterons exclude a statistical distribution of $O$ atoms.

Otherwise, the $v_O$ frequency should vary significantly with $p$, for $\Delta v_{OH}/\Delta R_p \approx 5000$ cm$^{-1}$ Å$^{-1}$ [22]. The absence of frequency shift, or band broadening, suggests that a mixed crystal can be represented by isomorphous sublattices $p[KHCO_3]$ and $(1 - p)[KDCO_3]$, whose structures and dynamics are independent of $p$. These sublattices are not resolved by diffraction.

3. Theory

Admittedly the enhanced features are evidence of quantum correlations, but different mechanisms have been envisaged: symmetry-related entanglement [12–15], quantum exchange [23] or spin–spin interaction [24]. They will be compared.

The Raman spectra suggest that the Hamiltonian for a mixed crystal can be partitioned as

$$H_p = p(H_H + H_{KHCO_3} + C_{KHCO_3}) + (1 - p)(H_D + H_{KDCO_3} + C_{D,KDCO_3}) + H_{ep}. \quad (3)$$

$H_H$ and $H_D$ represent the sublattices of $H^+$ and $D^+$; $H_{KHCO_3}$ and $H_{KDCO_3}$ those of heavy nuclei; $C_{KHCO_3}$ and $C_{D,KDCO_3}$ couple light and heavy nuclei. The sublattices are bound through the electronic term $H_{ep}$. There is no dynamical coupling between the KHCO$_3$ and KDCO$_3$ subsystems which are supposed to be separable; any state vector of $H_p$ is a tensor product of state vectors of the subsystems. Furthermore, the adiabatic separation of $H_H$ and $H_{KHCO_3}$, or $H_D$ and $H_{KDCO_3}$, leads to factorable state vectors for the subsystem of bare protons (fermions), or deuterons (bosons) [23–25]. The separation of proton and deuteron states is, therefore, consistent with the ‘superselection rule’ for fermions and bosons [26].

The mixed crystal is described by $N_a$, $N_b$, $N_c$ ($N' = N_aN_bN_c$) unit cells labeled $j, k, l$, along crystal axes $(a), (b), (c)$, respectively. The sublattices are described with the same unit cell containing $4p KHCO_3$ and $4(1 - p)KDCO_3$ entities. Proton/deuteron sites are organized in two dimer entities indexed as $j, k, l$ and $j', k, l$, respectively, with $j = j'$. For each dimer, dynamics are represented by normal...
coordinates, either antisymmetric $[\alpha_{\alpha}]$ or symmetric $[\alpha_{\alpha}]$ \((r = 1, 2, 3)\), which are linear combinations of displacements along \(x, y, z\), respectively. The coordinates of the centers of symmetry, \((\alpha_{\alpha}), (\alpha_{\alpha}')\), are \((x_0, y_0, z_0), (x'_0, y'_0, z'_0)\). For planar dimers, \(z_0 = z'_0 = 0\). Configurations \(LL\) and \(RR\) correspond to opposite signs for \(x_0\) and \(x'_0\). Although proton and deuteron sites may not be strictly identical, their dynamics are formally represented by the same set of normal coordinates.

The wavefunctions in the ground state are represented by Gaussian functions \(\Psi_{0;jkl}[\alpha_{\alpha}]\) and \(\Psi_{0;jklc}[\alpha_{\alpha} - \sqrt{2}\alpha_{\alpha}c]\), with \(C = 'LL'\) or \('RR'\).

A key issue of the theory is to clearly differentiate sites and states. Sites refer to local positional parameters, whereas each single state is extended over all indistinguishable sites. Conversely, the probability density (occupancy) at any site comprises contributions from every single state. The nonlocal observables (normal coordinates and conjugated momenta) are comprised of contributions from every single state. The nonlocality due to the lattice periodicity is not related to any physical interaction. It is energy-free. This is totally different in nature from the long-range quantum exchange in a supersolid, like the crystal of He [27]. Obviously, the proposal by Keen and Lovesey [23] that nonlocality could arise from phonons, (phonons), is incorrect, even for the ground state, this can be written as

\[
\mathbf{D}_{L_{\mathbf{c}}}^{\pm} = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} \sum_{k=1}^{N_i} \sum_{l=1}^{N_j} \sum_{m=1}^{N_j} (\Xi_{DJL_{\mathbf{c}}} C) \exp(\mathbf{i} \cdot \mathbf{L}_{ijkl} \cdot \tau); \quad (4)
\]

where \( \mathbf{i} \) is the wavevector; \( \mathbf{L}_{ijkl} = ja + kb + lc \) is a lattice vector; \( \mathbf{a}, \mathbf{b} \) and \( \mathbf{c} \) are the unit cell vectors. The wavefunctions for a unit cell, \( \Xi_{DJL_{\mathbf{c}}} C = \Theta_{DJL_{\mathbf{c}}} + \zeta \Theta_{DJL_{\mathbf{c}}} \) with \( \zeta = ' + ' \text{ or } ' - ' \), are a linear combination of the wavefunctions for centrosymmetric sites: \( \Theta_{DJL_{\mathbf{c}}} C = \prod_j \Psi_{0;jklc}(\alpha_{\alpha}) \) and likewise for \( \Theta_{DJL_{\mathbf{c}}} C = \prod_j \Psi_{0;jklc}(\alpha_{\alpha}) \). For centrosymmetric dimers, there is no permanent dipole, so long-range correlations through inter-dimer interactions are negligible. Phonons are virtually dispersion-free [20, 21].

\[
\mathbf{D}_{L_{\mathbf{c}}}^{\pm} = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} \sum_{k=1}^{N_i} \sum_{l=1}^{N_j} \sum_{m=1}^{N_j} (\Xi_{DJL_{\mathbf{c}}} C) \exp(\mathbf{i} \cdot \mathbf{L}_{ijkl} \cdot \tau); \quad (5)
\]

For each configuration \( C \), the ground states are entangled in position, momentum and spin. The singlet-like and triplet-like states are degenerate because the spin symmetry is energy-free. The proposal by Sugimoto et al [24] that the spin symmetry could be due to spin–spin interaction is incorrect because the actual coupling between nearest spin sites \((10^4 - 10^5)\) Hz–\(10^{-6}\) K is far too weak to give rise to long-lived correlations.

For an isolated crystal, symmetry-related quantum correlations are decoherence-free. Thanks to the adiabatic separation, there is no phonon-induced decoherence and, therefore, no transition to the classical regime, before melting or decomposition. In practice, some states can be transiently disentangled by external perturbations, such as thermal radiations, but this is counterbalanced by spontaneous re-entanglement via decay to the ground state. In a stable gaseous atmosphere, the density of the surroundings is \(1000\)-fold smaller than that of the crystal, so the impact of environment-induced decoherence on measurements is invisible. A source of disentanglement is the thermal population of excited proton states (for example, \( \gamma_0 \) OH and \( \gamma_0 \) OH at \(\approx 1000\) cm\(^{-1}\)), as the \(a - s\) splitting destroys the spin symmetry, but this is marginal.

Because the spin symmetry holds for both \( LL \) and \( RR \) ground states, for which there is no \( a - s\) splitting, the sublattice at 300 K can be represented by a mixture comprising a coherent superposition of super-rigid states for protons (5), on the one hand, and, on the other, a coherent superposition of phonon...
states for deuterons (4):
\[
|H^+(T)⟩ = \sum_\tau |q_{LH}^\tau(T)⟩|H^+_{LL}⟩ + q_{RRH}^\tau(T)⟩|H^+_{RR}⟩;
\]
\[
|D_k^\tau(T)⟩ = \sum_\tau |q_{LH}^\tau(T)⟩|D_k^+_{LL}⟩ + q_{RRH}^\tau(T)⟩|D_k^+_{RR}⟩;
\]
with \(|q_{LH}^\tau(T)⟩|^2 = q_{LH}(T)\), etc., in accordance with (1).

3.2. Neutron scattering

The partial differential nuclear cross section can be written as [30]
\[
\frac{d^2\sigma}{d\Omega dE} = \frac{k_t}{k_f} \sum_{1f} p_i |⟨\mathbf{k}_i|\tilde{V}(\mathbf{r})|\mathbf{i}⟩|^2 \delta(\hbar\omega + E_i - E_f).
\]

The summation runs over initial states \(|i⟩\), E\(_i\), weight \(p_i\) and final states \(|f⟩\), E\(_f\). The energy transfer is \(\hbar\omega\) and d\(\Omega\) is an element of solid angle. The interaction potential between the incident neutron and the target sample, \(\tilde{V}(\mathbf{r})\), comprises the interaction potential at every site. For diffraction, \(|i⟩ \equiv |f⟩\), E\(_i\) \equiv E\(_f\), \(\hbar\omega \equiv 0\). Neutrons are diffracted by each single state. Because of the adiabatic separation, neutrons diffracted by proton or deuteron states are free of any contribution from heavy atoms. Moreover, neutrons diffracted by proton states probe exclusively the interaction potential at the proton sites and likewise for deuteron states, irrespective of whether or not these sites are identical. There is no Laue monotonic diffuse scattering. In general, \(\tilde{V}(\mathbf{r})\) does not have the periodicity of the lattice, for the potential will depend upon the nuclear position and spin orientation. However, this is not the case for the super-rigid states which match exactly the periodicity of the crystal.

Upon momentum transfer to the target proton states (6), the final state is, in general, such that \(k_t \cdot L_{\|} \neq 0\) modulo 2\(\pi\), so elastic distortions are generated. They are represented by ellipsoids at H/D sites in figure 1. The super-rigid states are probed without induced distortions when
\[
\mathbf{Q} \cdot L_{\|} = 0 \text{ modulo } 2\pi.
\]

Then, neutrons probe the spin symmetry and the coherent cross section is the total nuclear cross section, \(\sigma_{H} \approx 82.0\) b, that is \(\approx 45\) times greater than the coherent cross section for regular Bragg peaks, \(\sigma_{H} \approx 1.8\) b, or \(\approx 15\) times greater than \(\sigma_{H} \approx 5.59\) b, or \(\approx 3\)-fold greater than \(\sigma_{KCOF} \approx 27.7\) b for heavy atoms. These scattering events emerge from the diffraction pattern with spectacular contrast, even at large \(|\mathbf{Q}|\) values as they are not attenuated by the Debye–Waller factor. Besides, they are temperature-independent.

For the \(P2_1/a\) structure, \(z\) is not parallel to an axis of the sublattice of protons (figure 1), so the matching condition (8) is never realized along \(Q_z\). The super-rigidity along \(z\) is necessarily destroyed by measurements and intensities are proportional to \(\exp -U_{zz}^2 Q_z^2\). On the other hand, since \(z_0 = z_0' = 0\) for planar dimers, the spin symmetry holds only in the \((x, y)\) planes, so the differential cross section for enhanced diffraction can be written as [14]
\[
\frac{d\sigma}{d\Omega} \propto \sum_{\tau} \sum_{k_{LL}} \sum_{j_{LL}} \sum_{i_{LL}} \exp iQ_{z} D_{z};
\]
\[
\times [\exp iQ_{y}(k D_{x} - \Delta_{y}/2) + \tau_{\tau_{\tau}} \exp iQ_{y}(k D_{y} + \Delta_{y}/2)]
\]
\[
\times \exp [-U_{zz} Q_{z}^2] \times \delta(\omega),
\]
where \([⋯]_2\) takes into account indistinguishable scattering events, either in-phase (\(|S⟩ \rightarrow |S⟩\) and \(|T⟩ \rightarrow |T⟩\)) or anti-phase (\(|S⟩ \rightarrow |T⟩\) and \(|T⟩ \rightarrow |S⟩\)). Enhanced diffraction by \((x, y)\) planes is anticipated at \(Q_{Hy} = \pm 2\pi n_{y}/\Delta_{x}\), \(Q_{Hz} = \pm 2\pi n_{z}/\Delta_{y}\) for \(n_{y}\) even (in-phase scattering) and \(Q_{Hz} = \pm 2\pi (2n_{z} + 1)/\Delta_{y}\), for \(n_{y}\) odd (anti-phase scattering). Then, enhanced Bragg peaks occur at \(Q_{z} \approx 2\pi n_{z}/\Delta_{y}\), with intensities proportional to \(\exp -U_{zz}^2 Q_{z}^2\).

Otherwise, if \(Q_{z} \neq 2\pi n_{z}/\Delta_{y}\), the super-rigid \((x, y)\) lattice is probed without distortion for the same \((Q_{Hz}, Q_{Hz})\) values, but the spin symmetry is destroyed. Incoherent scattering is observed and the intensity is proportional to
\[
\sigma_{H} \exp (-Q_{Hz} U_{zz}^2) \delta(Q_{x} - Q_{Hz} + Q_{y} - Q_{Hz}),
\]
hence the cigar-like shape. Compared to a nonrigid lattice, the enhancement is merely due to \(U_{zz}^2 = U_{zy} = 0\). The observed intensity ratio \(I_{0}/I_{10} \approx 2\) is at variance with the expected ratio of \(\approx 1.5\), but this discrepancy could be representative of errors in the background correction.

Figures 2–4 can thus be rationalized with three different kinds of scattering events: (i) regular Bragg diffraction by the crystal lattice; (ii) enhanced diffraction by the fully entangled sublattice of protons and (iii) incoherent scattering by the super-rigid planes of protons.

4. Discussion

The proposed theory is based upon fundamental laws of quantum mechanics applied to the crystal in question: the structure is periodic; dimers are centro-symmetric; indistinguishable protons are fermions; indistinguishable deuterons are bosons. It leads to macroscopically entangled states and, in the special case of protons, to super-rigidity and spin symmetry with observable consequences. This theory is consistent with a large set of experimental data (neutron diffraction, QENS, INS, infrared and Raman) and, to the best of our knowledge, there is no conflict with any observation. Therefore, every reason to conclude that the crystal is a macroscopic quantum system for which only nonlocal observables are relevant.

Because quantum entanglement emerges naturally from the crystal structure, there is no reason to introduce any further interaction. From the viewpoint of economy (Ockham’s razor), alternative theories based upon quantum exchange [23] or spin–spin interaction [24] are less satisfactory. Moreover, these correlations are very unlikely to be significant and it is doubtful that these short-range interactions, essentially confined to
dimmers, could account for macroscopic correlations, especially at elevated temperatures.

Protons are unique to demonstrating quantum entanglement, because they are fermions and because the very large incoherent cross section can merge into the total coherent cross section. No other nucleus can manifest such an increase of its coherent cross section. The enhanced features can be, therefore, unambiguously assigned to protons, in accordance with their positions in reciprocal space. They are evidence of macroscopic quantum correlations which have no counterpart in classical physics.

According to the theory, the pair correlation function for protons represented by ellipsoids in figure 1 are due to measurement-induced phonons. The structure free of induced distortions should comprise Dirac functions for protons and ellipsoids for deuterons. The spatial wavefunctions for protons (5) describe the distribution of the center of mass of the proton states with respect to that for all other atoms and the uncertainty principle holds at each site of the perfectly correlated sublattice.

It is widely believed that macroscopic objects are, in principle, governed by the laws of quantum mechanics and classical physics is an emergent phenomenon at an appropriate limit when the system interacts with an environment that might as well consist of its internal degrees of freedom [31]. The crystal of bicarbonate is a counterexample that is never amenable to classical physics, because (i) quantum entanglement is as robust as the crystal; (ii) the adiabatic separation insulates the proton states from every decoherence mechanism and (iii) the energy gap for excited proton states is much greater than $kT$.

A different approach places the emergence of classicality on the impossibility of distinguishing individual quantum levels with coarse-grained measurements [32]. Transposed to diffraction, the interaction potential in (7) is replaced by the mean potential, $V(\mathbf{r}) = \sum p_i |\langle i | V | i \rangle|$, which is then Fourier-transformed into the unit cell structure factor [30]. Eigenstates and nonlocal observables are thus translated into classical variables for particles located at definite sites and neutrons scattered by various nuclei can interfere, irrespective of whether or not these nuclei are involved in the same eigenstates. Because of the opposite signs of the scattering lengths for protons and deuterons, interferences could build up in such a way that some Bragg peaks would be more intense for KHCO$_3$ than for KDCO$_3$, or vice versa. However, these enhanced peaks are not expected to single out the reciprocal sublattice of protons and the structure factor does not account for the enhanced incoherent scattering along $Q_z$ in any way. In addition, the rigid-body analysis does not provide any evidence of correlation between protons and heavy atoms [12]. There is, therefore, experimental support to conclude that the assumption of classicality emerging from coarse-grained measurements is only a convenient approximation hiding the quantum nature of the crystal. Nevertheless, quantum effects embedded in the Bragg peaks transpire as the mean scattering length (2) is less satisfactory than the mixture of distinct sublattices (1), although the difference is not large enough to be firmly conclusive.

5. Conclusion

Neutron diffraction and Raman spectra show that the mixed isotope crystal is not a statistical mixture of KHCO$_3$ and KDCO$_3$ entities. The crystal is a macroscopic quantum system made of separable matter waves over the isomorphic sublattices of KHCO$_3$ and KDCO$_3$. The quantum theory shows that deuteron (boson) states can be represented by phonons whereas antisymmetrized proton (fermion) states demonstrate super-rigidity and spin symmetry. This macroscopic quantum entanglement is energy-free and decoherence-free. It is as robust as the crystal structure and the emergence of the classical regime at elevated temperatures is forbidden. The main outcome of the present work is that macroscopic quantum effects for protons are not destroyed by deuteron states. Despite their different masses, isotopes are not defects leading to localization, possibly because they are isoelectronic.

The quantum theory of diffraction by proton states allows us to distinguish different events. First, in the most general case, momentum transfer destroys the quantum entanglement and regular Bragg peaks are observed. Second, for those particular $Q$ values matching the nodes of the reciprocal sublattice, the super-rigidity and the spin symmetry are probed without any measurement-induced symmetry breaking. The incoherent cross section merges into the total coherent cross section and the corresponding peaks show markedly enhanced intensities featuring macroscopic quantum entanglement. Because of the anomalous Debye–Waller factor, these peaks are observed at large $Q$ values and they are temperature-independent. Third, for those $Q$ values matching only the nodes of the reciprocal planes of protons, the spin symmetry is destroyed and cigar-like shaped rods of incoherent scattering by the super-rigid planes are observed in between the enhanced peaks. Clearly, the unit cell structure factor is not appropriate to account for these enhanced features.

This work presents one single case of macroscopically entangled states on the scale of Avogadro’s constant in a mixed isotope crystal at room temperature. The quantum theory suggests that such macroscopic quantum effects should be of significance for many hydrogen-bonded crystals. Hopefully, unforeseeable consequences of the quantum view advocated in this work will appear in the future.

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