Direct Observation of Tunneling in KDP using Neutron Compton Scattering

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Neutron Compton scattering measurements presented here of the momentum distribution of hydrogen in KH_2PO_4 just above and well below the ferroelectric transition temperature are sufficiently sensitive to show clearly that the proton is coherent over both sites in the high temperature phase, a result that invalidates the commonly accepted order-disorder picture of the transition. The Born-Oppenheimer potential for the hydrogen, extracted directly from data for the first time, is consistent with neutron diffraction data, and the vibrational spectrum is in substantial agreement with infrared absorption measurements. The measurements are sensitive enough to detect the effect of surrounding ligands on the hydrogen bond, and can be used to study the systematic effect of the variation of these ligands in other hydrogen bonded systems.

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Hydrogen bonded ferroelectrics have been extensively studied for several decades. They are still of interest because of the continuing controversy over the nature of the phase transition, their technological importance, and their use as convenient systems in which to study hydrogen bonding. The most generally accepted interpretations of the transition mechanism in KH_2PO_4 (KDP) have ranged from order-disorder models involving only the protons [1] to models in which tunneling played an essential role [2] to order-disorder models involving the coupling of the protons to the polarization of the PO_4 groups [3,4]. It is known that in KDP [5] each proton is equally likely to be in either of two positions in the hydrogen bond above the ferroelectric phase transition at $T_c = 124$ K, where the structure is tetragonal, and is nearly entirely in one site below T_c, where the structure is orthorhombic. What has not been known, and has been a subject of controversy since Blinc [2] proposed the idea in 1960, is whether the protons are tunneling between the two equivalent sites or are localized in one or the other of the two sites and simply disordered above the transition. While the tunneling model was used to describe the data for some time after it was proposed, Raman scattering data [6] that seemed to show that the symmetry of the surroundings of the proton did not change above and below the transition, together with subsequent neutron scattering results [7], led to the consensus that the proton was self-trapped in one or the other of its equivalent positions, and jumped from position to position through phonon assisted tunneling. If such a picture were correct, the proton would be in one site or the other in the high temperature phase for times much longer than the time scale of our experiment (10^{-15}–10^{-16} sec), not simultaneously in both. The transition would be an order-disorder type in which the populations of the two sites became unequal below the ordering temperature. As pointed out by Reiter and Silver [8], neutron Compton scattering (NCS)provides a means to distinguish between models in which the proton is coherent over both sites and the order-disorder models in which it is in one site or the other. If the latter were correct, NCS should see only a small change in the momentum distribution. This would be due to whatever changes occurred in going through the transition to the potential of individual wells in which the proton was trapped. By contrast, if the particle were tunneling, that is, coherent over both sites, and then became trapped, we should see a narrowing of the momentum distribution in the tunneling phase, together with an oscillation due to the coherent interference of the proton in the two sites. We show here that the distributions at temperatures above and below the ferroelectric transition are, in fact, dramatically different, and consistent with the proton coherently occupying the two sites. Since the bond is symmetric above the transition, one can construct the effective Born-Oppenheimer potential directly (without any model) from the measurement of the momentum distribution [8]. This is, as far as we know, the first such measurement of a Born-Oppenheimer potential in any system. It yields a double well potential with parameters consistent with neutron crystallography and incoherent neutron scattering at lower scattering energies, and yields vibration frequencies consistent with infrared measurements.

The experiments are done on the electron volt spectrometer, EVS, at ISIS, the pulsed neutron source at the Rutherford Laboratory. This sort of source is needed to provide high energy neutrons (5–10 eV) for which the energy transfer is sufficiently large compared to the characteristic energies of the system that the scattering is given accurately by the impulse [9] approximation limit. The scattering at these energies is entirely incoherent, each particle scattering independently. $S_M(\vec{q}, \omega)$, the scattering function for a particle of mass M, is related to the momentum distribution of the particle $n(\vec{p})$ in this limit by the relation

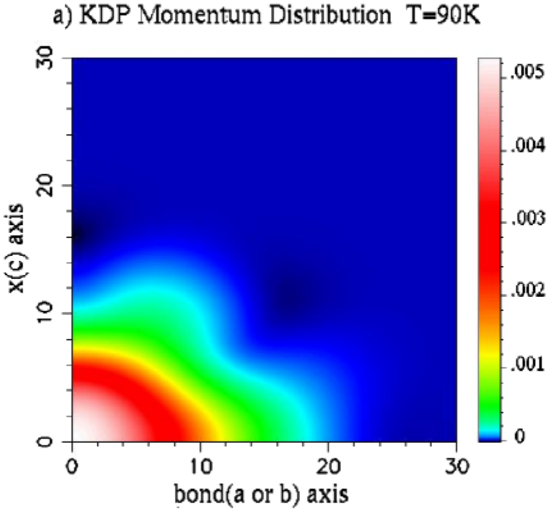
$$S_M(\vec{q}, \omega) = \int n(\vec{p})\delta\left(\omega - \frac{\hbar q^2}{2M} - \frac{\vec{p}.\vec{q}}{M}\right)d\vec{p}, \tag{1}$$

where $\hbar\omega$ is the energy transfer, M is the mass of the proton, and $q = |\vec{q}|$ is the magnitude of the wave-vector transfer.

The small mass of the proton leads to a broad distribution in energy of the scattered neutrons, centered at $\frac{\hbar^2 q^2}{2M}$, that is well separated from the scattering from the heavier ions such as oxygen, which appear as nearly elastic contributions. This, together with its large incoherent cross section, makes it an ideal candidate for these measurements. $n(\vec{p})$, the probability of observing the proton with momentum $\vec{p}$, for simple one particle systems in their ground state, is the square of the absolute value of the Fourier transform of the spatial wave function. The experimental data are fit in a model-free way using a series expansion that allows one to reconstruct $n(p)$ directly from the fitted coefficients. We represent $S_M(\vec{q}, \omega)$ as $\frac{M}{q}J(\hat{q}, y)$ where $y = \frac{M}{q}(\omega - \frac{q^2}{2M})$, and expand $J(\hat{q}, y)$ as

$$J(\hat{q}, y) = \frac{e^{-y^2}}{\pi^{1/2}} \sum_{n,l,m} a_{n,l,m} H_{2n+l}(y) Y_{lm}(\hat{q}), \tag{2}$$

where the $H_n(y)$ are Hermite polynomials and the Y_{lm} are spherical harmonics. This series is truncated at some order ($2n + l = 10$ in this case), convolved with the instrumental resolution function and then least-squares fit to the data. The coefficients $a_{n,l,m}$ then determine the measured $n(\vec{p})$ directly as a series in Laguerre polynomials and spherical harmonics [8,10]. The procedure is a smoothing operation, which works with noisy data, and which also allows for the inclusion of small corrections to the impulse approximation [10,11]. The errors in the measured $n(\vec{p})$ are determined by the uncertainty in the measured coefficients, through their correlation matrix, which is calculated by the fitting program. For an expanded discussion of the procedure and errors, see Ref. [10]. In fitting the data, we take the z axis to be along the bond axis, the x axis to be the c axis of the crystal, perpendicular to both bonds, and fit the data with the sum of two terms, one rotated by 90° about the x axis from the other. The measurement provides the complete 3D momentum distribution. We show in Fig. 1 a cut along the p_x-p_z plane for the momentum distribution of a single bond at two temperatures, one far below and one just above the transition. The measurements were taken with exactly the same experimental configuration, and analyzed with exactly the same terms kept in the series expansion. If the order-disorder picture of the transition had been correct, we would expect to see small changes in the momentum distribution on going through the transition, as the proton would remain localized in one or the other equivalent sites, and the confining potential at that site would be only slightly modified. In fact, we see dramatic changes in the width and the shape of the momentum distribution. While there is little change in the direction normal to the bond, the distribution along the bond changes qualitatively.



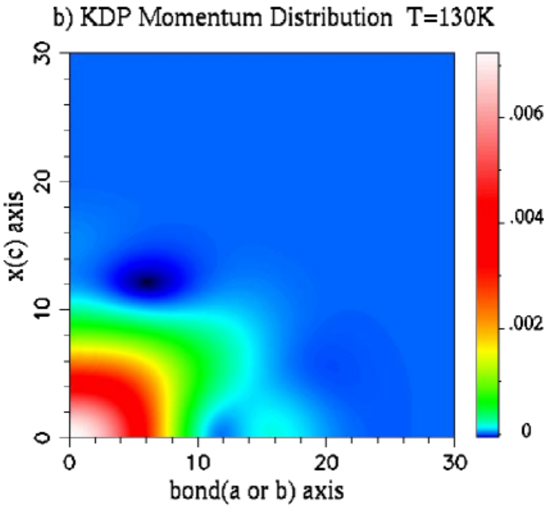


FIG. 1 (color online). The momentum distribution in the p_x-p_z plane for a single hydrogen bond (a) below ($T = 90$ K) and (b) just above ($T = 130$ K) the ferroelectric transition at $T = 124$ K. The bulge in (b) along the direction roughly 30° from the bond axis, that is, the projection of the displacement from the center of the bond to the phosphorus ion, is interpreted as being due to the repulsion of the proton by the phosphorus.

The momentum distribution along the bond axis for both temperatures is shown in Fig. 2. The dotted lines give the uncertainty in the distribution function as a result of the uncertainty in the measured coefficients.

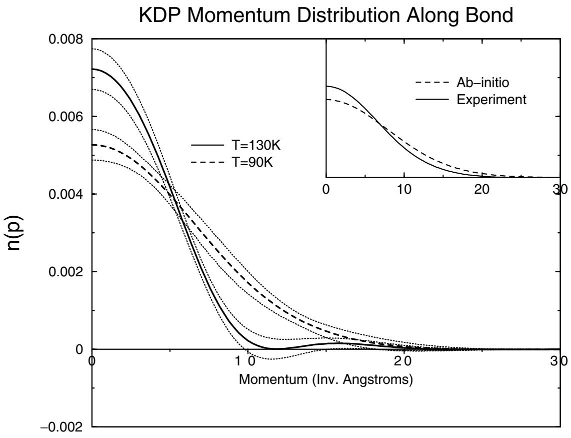


FIG. 2. The momentum distribution along the bond axis for temperatures just above and well below the structural phase transition at 124 K. The dotted curves surrounding the heavy lines are 1 standard deviation error markers. The inset is a comparison of the measured momentum distribution at $T = 90$ K with a recent calculation by Koval, Kohanoff, and Migoni [15] in which their *ab initio* one particle potential along the bond was used to calculate the momentum distribution from the one-dimensional Schrodinger equation, assuming the three-dimensional potential was separable.

We see that overall there is considerable narrowing of the distribution in the high temperature phase, indicating an increase in the length along the bond over which the spatial wave function is coherent. The prominent feature of the high temperature distribution, the zero, and the subsequent oscillation, is precisely what one would expect for a spatial wave function that was coherent over both sites, with the position of the zero being determined by the separation of the sites.

The momentum distribution contains many-body effects due to the motion of the surrounding ions. These effects are quite small for the heavy ions [12], but could be significant for the interaction of the protons with themselves. If we treat these interactions in a mean field approximation, we can calculate an effective one body Born-Oppenheimer potential from the momentum distribution in the high temperature phase, assuming the proton is in its ground state [8]. We will assume the potential is separable to simplify this calculation, so that we need only the data along the p_z axis.

The error bars on the measurements are such that there is considerable uncertainty in the tail of the distribution, and one could argue that there is no oscillation. If, however, we take the zero of the most probable distribution to be real, and choose the sign of the wave function as negative for momenta greater than the momentum at the zero, then we find the effective Born-Oppenheimer potential and the spatial wave function shown in Fig. 3. If we do not change the sign, we get a completely unphysical potential. It is clear that the most likely momentum distribution measured supports a tunneling model. The tunnel splitting is 94 meV ($\sim$ 1000 K), so that our assumption that we are seeing only the ground state is consistent. The value for the tunnel splitting is larger than most earlier experimental estimates [13], which have a maximum value of about 60 meV. It is very sensitive to the height of the barrier. We estimate the error on this number to be at least 20%, perhaps as much as 40%. Even if one does not take seriously the oscillation in the tail of the momentum distribution, and assumes that the actual distribution goes smoothly to zero, we would find a much broader potential above T_c than below, and the order-disorder model would be equally untenable. That potential would, however, be inconsistent with the neutron crystallography [5], which clearly shows a double peak structure for the spatial wave function, as in Fig. 3.

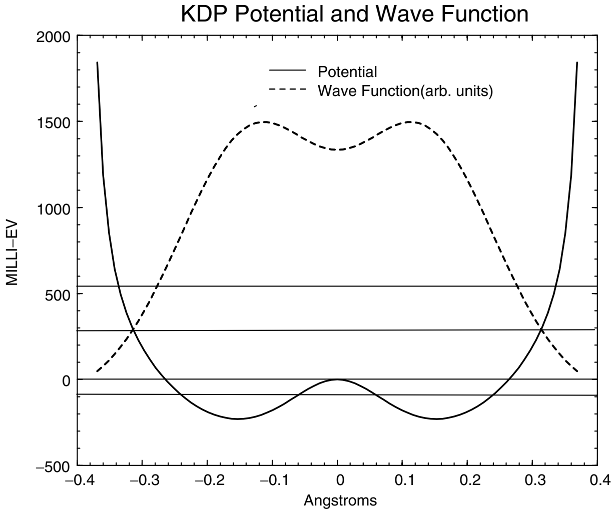


FIG. 3. The effective Born-Oppenheimer potential that corresponds to the measured momentum distribution along the bond at $T = 130$ K (Fig. 2), together with the spatial wave function for that potential. The horizontal lines give the first four energy levels for the measured potential.

Although the potential in Fig. 3 is quite different from that inferred from infrared absorption data by Lawrence and Robertson (LR) [13] who assumed that it could be described by back-to-back Morse potentials, the transition energies they based the fit on are substantially the same as those in the figure. LR identify the $0 \rightarrow 3$ transition as having an energy of 4600 cm^{-1}, whereas we obtain 5088 cm^{-1}. For the $1 \rightarrow 2$ transition, LR obtain 2260 cm^{-1}, while we obtain 2039 cm^{-1}.

We note that an earlier NCS experiment at KENS [14], done with much smaller count rates and using only a single detector, failed to detect the expected difference between the high and low temperature momentum distributions. This may have been because they did not take into account the variation of the angle the transferred wave vector makes with the crystal axes as the time of flight varies, which would have reduced the effect they would expect to see. More of the sampling would be from directions perpendicular to the bond, which do not change significantly. But even with our improved statistics, we would have found it difficult to see the difference between the distributions at high and low temperatures in a single time of flight data set visually. It is only by combining data from multiple orientations of the crystal and many detectors that the full picture of the momentum distribution emerges [10].

Neutron crystallography studies have fit the shape of the spatial wave function with the sum of two displaced Gaussians, which would give a rather different potential than that of Fig. 3, and obtained a separation of the minima of the potential, of 0.34 Å. We find 0.31 Å for this separation. The shape of the spatial wave function in Fig. 3 is qualitatively similar to that described in Ref. [5]. We conclude that the potential of Fig. 3 is at least qualitatively correct, and that the proton is indeed tunneling between equivalent sites in the high temperature phase.

Below the transition, since the potential is not symmetric, it is not possible to invert the data to obtain it, as phase information is lost in the momentum distribution. If one has a prediction for the potential, one can, however, calculate the momentum distribution. In the inset of Fig. 2, we show the momentum distribution obtained from a recent [15] *ab initio* calculation of the Born-Oppenheimer potential for KDP in which the electronic many-body problem was treated by density functional theory. The one particle approximation is evidently reasonably good here.

Along the directions perpendicular to the bond, the data are well fit by Gaussians at 130 K, are somewhat less well fit at 90 K, and change very little with temperature, in agreement with elastic incoherent scattering [16] and infrared [17] measurements. The harmonic frequencies obtained from our fits at 130 K are 1234 cm^{-1} for vibrations along the y axis, and 1015 cm^{-1} along the x axis, as compared to the infrared results of 1293 and 1038 cm^{-1}, respectively.

If a hydrogen bond were isolated, the momentum distribution would have to be symmetric about the bond axis. We find that distribution in the p_x-p_y plane (not shown here) is significantly broader at 45° to either axis than it is along the axes. This direction is approximately the projection in the x-y plane of the vector from the center of the bond to the phosphorus ion [18]. If we return to Fig. 1, we see that there is also a broadening of the distribution in the high temperature phase at approximately 30° to the z axis, which is the approximate direction of the projection of the vector from the center of the bond to the phosphorus ion on the x-z plane. This broadening becomes a narrowing at low temperatures. We conclude that this broadening in momentum space is a result of the repulsion of the proton by the phosphorus ion, and that the transition displaces the particles in a way that reduces that repulsion. This is in broad agreement with both the calculation cited above and another recent *ab initio* calculation [19] that showed that the motion of the phosphorus had large effects on the hydrogen potential surface. These observations, together with the large tunnel splitting, which reduces the significance of the tunneling on the transition, tend to support models in which it is the coupling to the polarization of the PO_4 complex that drives the transition [4], not the interaction between the protons, as in Blinc's original tunneling model.

We conclude that the experiments are easily sensitive enough to see the effect of the surrounding ions on the hydrogen bond, and include many-body effects that are difficult to calculate with existing methods. This sensitivity opens up the possibility of studying the effect of the systematic variation of the surrounding ligands on the dynamics of hydrogen bonds. The knowledge gained could then be used to identify the best models and *ab initio* approximation schemes, and to infer the behavior of the bonds in environments where the measurements cannot be done because there are two many inequivalent hydrogens, such as in DNA or proteins.

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