

Quantum aspects of low-temperature properties of crystals: A calorimetric study in interaction with spectroscopy and diffraction*

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Abstract: Some of the molecular and ionic crystals containing hydrogen undergo phase transitions only when they are deuterated. This indicates that not only the intermolecular potential energy, but also the kinetic energy of the nuclei are involved in an essential way in the mechanisms of the transitions. The quantum effects implied by these observations are discussed in terms of tunneling of protons and deuterons. Experimental evidence for deuteration-induced phase transitions and nuclear tunneling states accumulated by low-temperature calorimetry, far infrared spectroscopy, and neutron diffraction is discussed.

INTRODUCTION

Quantum theory is the fundamental principle on which we base our endeavor to understand Nature. The theory was conceptually difficult when the original thinkers M. Planck, N. Bohr, A. Einstein, M. Born, W. Heisenberg, and E. Schroedinger conceived it in various forms at the beginning of the 1900s. Now, 100 years later, it is still counterintuitive, even though all the applications of the theory to concrete physical and chemical problems have invariably produced remarkably accurate answers [1,2]. We are accustomed to accurate calculations of the electronic energy of molecules based on quantum mechanics and, following the probability interpretation of the wave function, visualize electrons in a molecule as a fuzzy cloud of probability density surrounding the nuclei.

For the motion of atomic nuclei, the most common situation in physical chemistry is the quantized energy levels of a harmonic oscillator. This gives rise to familiar vibrational spectra and forms the basis for the Einstein and Debye theories of the heat capacity of solids. The motion of nuclei is thus evidently quantized. However, we tend to think of nuclei as charged stationary mass points. This is a satisfactory approximation in the vast majority of situations we encounter in the physical chemistry of condensed matter. Also, the harmonic oscillation is a familiar type of motion in classical mechanics, and the main features of its classical description are carried over to the quantum description. However, there is a peculiar type of motion, the tunneling motion, in quantum mechanics that has no counterpart in classical mechanics. In gas-phase molecules to which high-resolution spectroscopy is applicable, nuclear tunneling states have been identified in various systems [3–5]. This has extended the originally studied inversion tunneling of an ammonia molecule [6].

In ferroelectrics, tunneling states of protons in short hydrogen bonds were introduced in 1957 to explain the remarkable difference in the transition temperature of potassium dihydrogen phosphate and

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its deuterated analog [7], but the idea has been difficult to maintain in the absence of experimental evidence for the tunneling states.

Atomic tunneling is invoked when the reaction rate becomes independent of temperature at low temperature where bare tunneling of atoms in the ground state determines the observed reaction rate [8]. Actually, the tunneling may be more prevalent in thermally populated states than in the ground state, but this cannot be shown easily because the distinction between the quantum and thermally activated processes is difficult to distinguish at higher energies. In living systems, the rate of biological reactions, such as the oxidation of cytochrome, becomes independent of temperature at low temperatures [8], supporting the involvement of the quantum effect.

The quantum nature of matter has been discussed in vastly different contexts remote from chemistry and physics. In our thought process, the quantum principle may play a fundamental role as Bohm speculated in 1951 [9] and Chalmers in 1996 [10]. The same point of view was advanced from a structural study of nervous cells of animals including us [11], and from analysis of the functioning of our brain [12]. If the tunnel effect and the quantum mechanics in general are important in chemical reactions and in life processes, obviously it has to involve the wave functions of the atomic nuclei forming the chemical and biological systems, not just the wave functions of the electrons belonging to the molecules.

In general, there are three stages of quantum effect: (1) the energy quantization, (2) delocalized wave functions, and (3) the symmetry of the states against exchange of identical particles. We are familiar with the first through vibrational spectroscopy and the low-temperature heat capacity of solids as we have noted above, whereas the third aspect is important in the rotational states of methane molecules and ammonium ions and uni-axial rotation of methyl groups and coordinated ammonia molecules [13]. In the present article, we are mostly concerned with the second aspect of the quantum effect of the *nuclear* motion.

Our interest in this problem arises from a basic question: To what extent are atomic nuclei delocalized, and do spatially extended wave functions determine the bulk properties of matter in different ways to those expected from their classical mass point picture? A proton is 1836 times, and a deuteron 3675 times, more massive than an electron. Despite the large masses of these particles, we have found that the quantum nature of their motion appears in a rather interesting way in the properties of crystals.

DEUTERATION-INDUCED PHASE TRANSITIONS

Properties of a crystal containing hydrogen change in different ways when it is deuterated, depending on the chemical state of the hydrogen atom in the compound. Most commonly, frequencies of normal modes of molecular vibrations decrease. For a harmonic oscillator, the decrease is at most by a factor of the square root of 2. Usually, it is much less than this because atoms other than those of hydrogen take part in the vibration. The decreased normal mode frequencies give the deuterated compound a larger heat capacity than the corresponding undeuterated compound. All the thermodynamic properties, including the free energy, change accordingly. This type of a mass effect is experimentally confirmed, as shown in Fig. 1 for malonic acid and malonic acid-d₄ [14]. Melting and phase-transition temperatures also change on deuteration. However, they are not directly related with the isotope effect in the vibrational free energy, because the mass difference changes the free energies of the two phases more or less similarly. Deuteration increases the melting point of ice only by 1.5 % even though the hydrogen bonding is entirely responsible for solidification. In malonic acid, the deuterium substitution decreases the melting point from 352.2 to 348.0 K, whereas the transition temperature increases from 47.3 to 60.0 K [14].

Although these weaker forms of the isotope effect are of interest from physical and chemical points of view, and their mechanisms have not been understood at all, we are concerned in this article with a more drastic deuteration effect. Some deuterated crystals undergo phase transitions while the corresponding undeuterated compounds do not. Phase transitions undergone only by deuterated com-

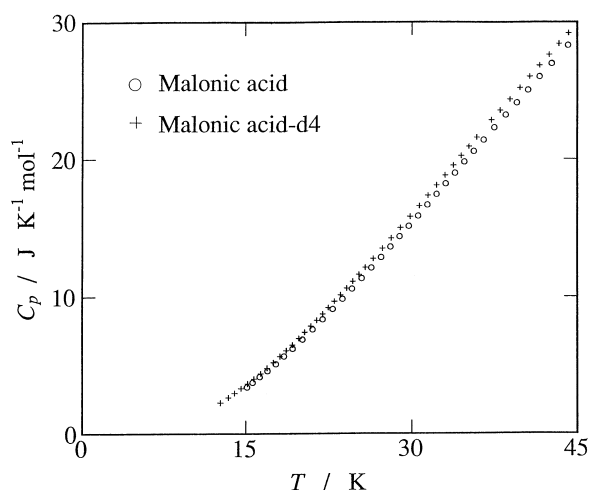


Fig. 1 Low-temperature heat capacities of malonic acid and malonic acid-d4 showing the normal deuteration effect on the vibrational heat capacity [14].

pounds are evidence for the quantum nature of nuclear motion (especially for protons and in certain cases for deuterons as well). The reason for this is as follows. On a very general thermodynamic basis, a phase transition occurs when one of the phases has a low energy and low entropy and the other phase has a high energy and high entropy. The former is stable at low temperature, and the latter at high temperature. However, the molecular interaction is determined by the electronic states, and the electronic states do not depend on the mass of the nucleus to a good approximation, as Born and Oppenheimer showed [15]. Hence, nuclear masses do not enter in the potential energy between molecules and in the mechanism of a phase transition. The mass dependence can be introduced through nuclear tunneling [7]. Deuteration-induced phase transitions are thus clear evidence for the quantum nature of atomic motion for which the simple mass effect on harmonic vibrations cannot give adequate explanations.

The experimental methods we use are low-temperature calorimetry, infrared spectroscopy, and neutron diffraction. The first is powerful in detecting and characterizing phase transitions. Infrared absorption gives immediate evidence for tunneling levels (and their absence) when the spectra of normal and deuterated compounds are compared. The role of neutron diffraction is unique and decisive in the present context since it gives the spatial extension of the nuclear distribution. Its distinction from X-ray diffraction is important: The neutron is scattered by nuclei, whereas X-ray scattering is by electrons. It is also important that coherent scattering amplitudes of hydrogen and deuterium are comparable with those of much more massive nuclei such as chlorine and platinum. While X-rays scattered by heavy atoms (chlorine, platinum, and others) overshadow those scattered by hydrogen atom, the light and heavy atoms scatter neutrons more or less with similar intensities, so that the positions of hydrogen atoms can be determined much more accurately by neutron diffraction. Also, the technical progress in data analysis has been helpful: recent development of the maximum entropy method is ideally suitable for the present purpose of determining detailed distribution of atomic nuclei.

SUBSTITUTED HYDROXYPHENALENONE

Anomalous properties of bromohydroxyphenalenone at low temperature were first reported by Mochida et al. by dielectric measurement [16]. We measured the heat capacities of normal and deuterioxy compounds BHP and BDP, respectively, (see Fig. 4 for the molecular structure) and found two phase transitions at 21.3 and 33.9 K for the latter and no anomalous heat capacity at all for the former [17]. The anomalous heat capacity is shown in Fig. 2, as determined after evaluation of the vibrational heat ca-

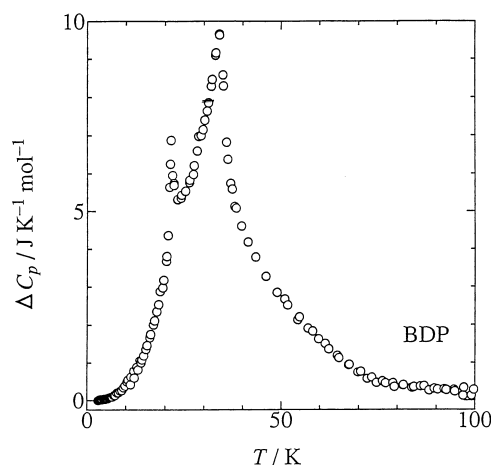


Fig. 2 The excess heat capacity of bromodeuterioxyphenalenone (BDP) due to phase transitions [17].

capacity. The two peaks correspond well with the dielectric anomalies and have been explained as arising from a normal (high temperature) to incommensurate (33.9 K) and incommensurate to ordered (21.3 K) phase changes [18]. The total entropy of transition is $6.8 \text{ J K}^{-1} \text{ mol}^{-1}$. The high-temperature phase is thus disordered in a classical way (cf. $R \ln 2 = 5.76 \text{ J K}^{-1} \text{ mol}^{-1}$). The disorder occurs in the intramolecular O–D–O bond. The deuteron positions become ordered through two phase transitions. The ordered structure has not been determined. Interestingly, the heat capacity of BHP is larger than that of BDP for 60–100 K [17]. This can only be understood by assuming extra energy levels present only in BHP. We remember that an opposite change is expected from the normal vibrational isotope effect discussed above. With a considerable effort to separate the excess part from the large phonon heat capacity, we determined the extra energy level at 64 cm^{-1} above the ground state. Figure 3 shows the excess heat capacity of BHP and the best-fit Schottky heat capacity. Thus, at higher temperature, the deuteron in the O–D–O bond of BDP occupies at random one or the other of the double minima of the potential energy, while for the proton in BHP, the two states corresponding to the two minima are split into separate states of symmetric and antisymmetric combinations of the two localized states. The tunnel splitting is

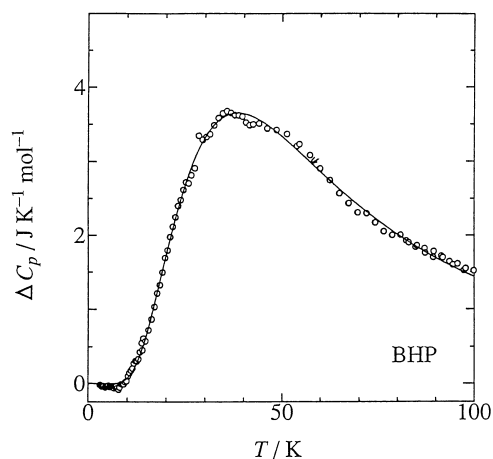


Fig. 3 The excess heat capacity of bromohydroxyphenalenone (BHP) due to a pair of tunnel states [17].

64 cm^{-1} . As the temperature decreases, more and more protons occupy the ground state without causing any discontinuity in the property of the crystal. Thus, the third law of thermodynamics is obeyed as a result of ordering of the positions of deuterium in BDP and by gradually increasing occupation of the ground state in BHP.

The tunneling level introduced to explain the excess heat capacity of BHP was found by infrared spectroscopy. In Fig. 4, the far infrared spectra of BHP and BDP are shown for temperatures between 5 and 300 K [19]. The strong absorption occurring at 83 cm^{-1} for BHP is entirely absent from the spectra of BDP, while other peaks (due to intra- and intermolecular vibrations) appear approximately at the same wave numbers with similar intensities. The temperature dependence of the 83 cm^{-1} absorption is also distinctly different from that of the other peaks. The wave number increases with temperature, unlike ordinary vibrational transitions, while the intensity decreases rapidly as the temperature increases. The intensity behavior is understood by considering the occupation number of the ground state, which decreases with increasing temperature. The difference ($64\text{ vs. }83\text{ cm}^{-1}$) in the energies from calorimetry and spectroscopy arises from the approximation involved in the analysis of the calorimetric data.

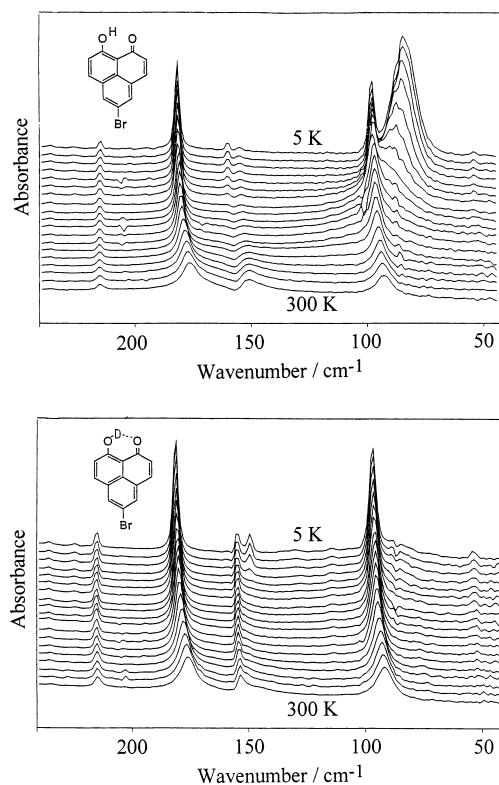


Fig. 4 Far infrared spectra of BHP (upper) and BDP (lower) showing a strong absorption at 83 cm^{-1} for the former and no corresponding absorption for the latter [19].

That BHP is not an isolated exceptional case is shown by the same type of infrared absorption in iodohydroxyphenalenone (IHP) [20]. The tunneling absorption occurs at 68 cm^{-1} in IHP with similar temperature dependence of the peak wave number and intensity. Two points are worth noting about the tunneling peaks. They are extraordinarily strong, being 4–6 times as strong as nearby intense vibrational peaks. This is related to the large spatial extent of the tunneling wave functions compared with more

compact Gaussian wave functions of the vibrational ground state. The large amplitude of the wave functions (of the ground and excited states) away from the origin of the coordinate gives a large matrix element connecting the ground and excited states and hence the strong intensity of the tunneling peak (see Fig. 5). The second point to be noted is the difference of the tunnel splitting of BHP and IHP. Other peaks of the two compounds occur at nearly the same wave numbers, but the tunnel peaks are significantly different (83 and 68 cm^{-1}). This indicates the sensitivity of the tunnel splitting to the potential energy, depending critically on the barrier height and width separating the two minima. An interesting theoretical paper has been published by Totsuji and Matsubara. They treated both the electron and proton quantum mechanically and found that, for certain values of parameters, the hydrogen bonds are tunneling at 0 K while deuterium bonds are ordered [21].

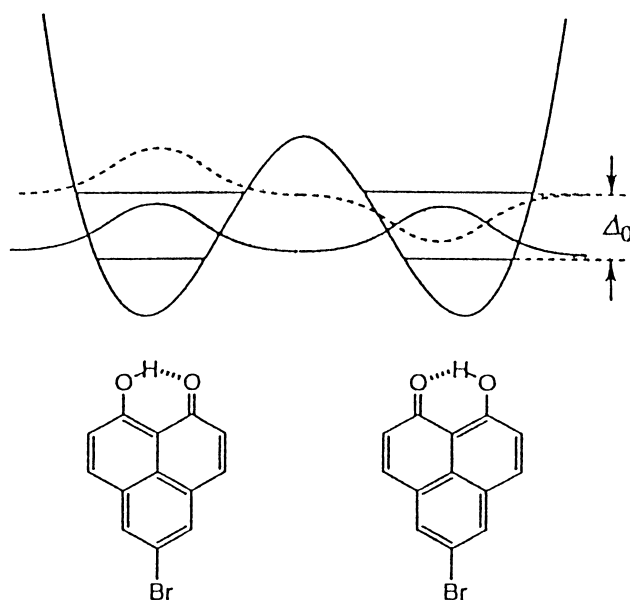


Fig. 5 Schematic presentation of a double minimum potential for the proton in the intramolecular hydrogen bond of BHP. Wave functions of the ground and excited states are also shown.

TRIALKALI HYDROGEN (DEUTERIUM) DISULFATES AND DISELENATES

This group of hydrogen-bonded crystals undergo phase transition when deuterated. The heat capacity peaks were analyzed by the use of an extended least-squares fitting of the vibrational transitional heat capacities and has been presented in the poster session of the ICCT 2002 for $\text{Rb}_3\text{D}(\text{SO}_4)_2$ [22]. For the cesium selenate system, the hydrogenous crystal $\text{Cs}_3\text{H}(\text{CsO}_4)_2$ undergoes a phase transition at 53.3 K , and the deuterated crystal $\text{Cs}_3\text{D}(\text{SeO}_4)_2$ at 171.5 K (Fig. 6 [23]).

We determined the anomalous heat capacities by the extended least squares and from them the entropy of transition $1.5\text{ J K}^{-1}\text{ mol}^{-1}$ for $\text{Cs}_3\text{H}(\text{CsO}_4)_2$ and $5.2\text{ J K}^{-1}\text{ mol}^{-1}$ for $\text{Cs}_3\text{D}(\text{SeO}_4)_2$ [24]. We interpret this result as indicating that the deuterated compound is effectively a classical order–disorder crystal, whereas the hydrogenous compound is a quantum order–disorder compound in which proton tunnel splitting is significant in the high-temperature phase. Deuteration-induced phase transitions occur also in $\text{Rb}_3\text{D}(\text{SeO}_4)_2$ [25] and $\text{K}_3\text{D}(\text{SO}_4)_2$ [26].

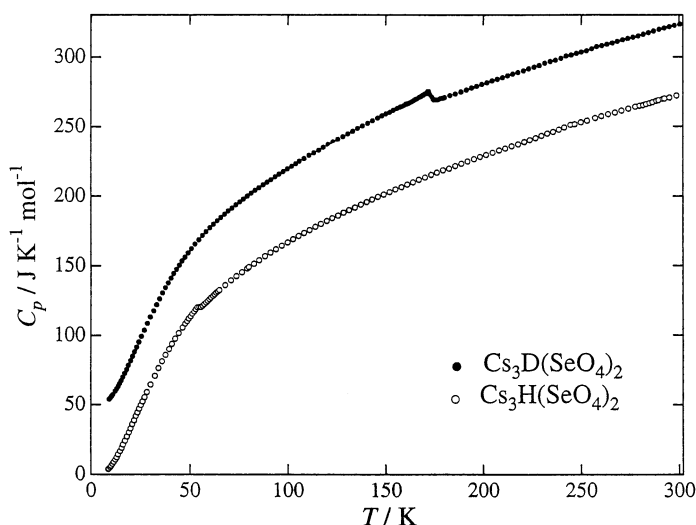


Fig. 6 The heat capacity curves of $\text{Cs}_3\text{H}(\text{SeO}_4)_2$ and $\text{Cs}_3\text{D}(\text{SeO}_4)_2$, showing a strong deuteration effect on the phase transitions. $T_c(\text{D}) = 171$ K, and $T_c(\text{H}) = 53$ K [23].

DIAMMONIUM HEXACHLOROMETALLATES OF THE POTASSIUM HEXACHLOROPLATINATE STRUCTURE

Weir and coworkers measured the heat capacity of a series of these ammonium compounds and their deuterated analogs [27] and found phase transitions in many of them. We also measured the heat capacity of some of the compounds of the same series and analyzed the results in some detail [28–30]. An interesting point about these phase transitions is that the transition entropy varies considerably for different compounds ($7.5 \text{ J K}^{-1} \text{ mol}^{-1}$ for $M = \text{Pb}$ and $16.6 \text{ J K}^{-1} \text{ mol}^{-1}$ for $M = \text{Pd}$) even though the transition temperatures are in a narrow range of 30–40 K. It is also significant that the deuteration-related transitions are sharp first-order transitions. Consequently, evaluation of the transition entropy from the experimental heat capacity data is a straightforward procedure demanding no special device for determination of the lattice heat capacities. We interpreted the different values of the transition entropy as arising from Schottky entropies truncated by first-order transition at different temperatures [30]. We suppose that ND_4^+ ions are disordered in the high-temperature phases. This is not a trivial assumption by itself, given the same symmetry Td of a free ammonium ion and that of the site $(1/4, 1/4, 1/4)$ it occupies in the K_2PtCl_6 structure. But it must be orientationally disordered in view of the large transition entropy values. We suppose further that the barrier separating the disordered states is small so that the ND_4^+ ion is able to tunnel from one orientation to another quantum mechanically. The tunneling gives rise to split energy levels, as we have discussed for O–H–O hydrogen bonds. The energy levels generate a Schottky heat capacity as shown in Fig. 7. However, the Schottky anomaly is truncated by the phase transition, as also shown in Fig. 7. Thus, the entropy contained in the Schottky heat capacity below the transition temperature is acquired by the crystal discontinuously at the transition temperature as a latent heat of transition.

Figure 7 also explains the experimental results that for some of the compounds ($M = \text{Pt}$, Pb , and Te) the heat capacity of the high-temperature phase is significantly larger than that of the low-temperature phase. We determined the Schottky levels from the temperature and entropy of the transitions. The Schottky levels thus determined are correlated smoothly with a structural parameter (the $M\text{--Cl}$ distance) giving support to this analysis (Fig. 8).

Further support for the Schottky model is found in the comparison of the heat capacities of $(\text{NH}_4)_2\text{IrCl}_6$ and $(\text{NH}_4)_2\text{SnCl}_6$ with those of the respective deuterated compounds. These four crystals

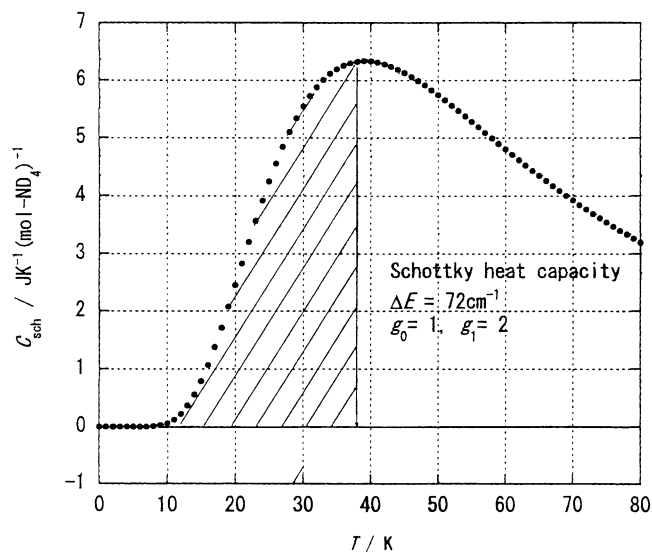


Fig. 7 The Schottky heat capacity and its truncation by a first-order phase transition. The energy level splitting may be determined by fitting the heat capacity curve itself or by comparison of the experimental and calculated values of the transition entropy.

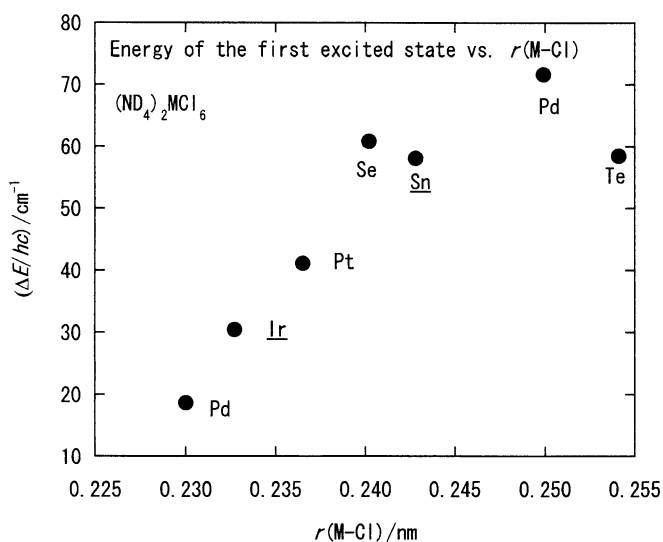


Fig. 8 Correlation between the tunnel splitting and the (M-Cl) distance for $(\text{ND}_4)_2\text{MCl}_6$. More recent data are added to [30].

remain cubic down to the lowest temperature (we studied to 5 K). The heat capacities of the deuterated crystals are considerably larger than those of the hydrogenous crystals. The difference plotted in Fig. 9 is reproduced well by a 1:2 Schottky heat capacity curve.

It has to be taken into account that there are two ammonium ions in the chemical unit. The energy levels thus determined from the heat capacity are also on the same curve in the splitting vs. $r(\text{M-Cl})$ plot (Fig. 8). The iridium compound is particularly interesting: the splitting is small (corresponding to a large excess heat capacity at low temperature), hence, ND_4^+ is close to a disordered clas-

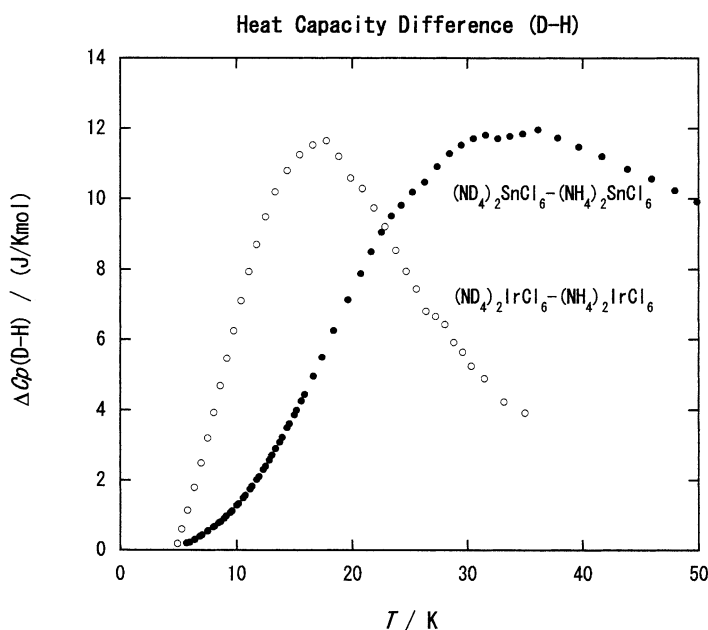


Fig. 9 The D–H difference of the heat capacities of $(\text{NH}_4)_2\text{IrCl}_6$ and $(\text{NH}_4)_2\text{SnCl}_6$.

sical rotator and yet it maps out an entire Schottky curve, giving clear evidence for the rotational tunneling of the ND_4^+ ion. NH_4^+ ions also tunnel, but the tunnel splitting is so large that the upper levels are not sufficiently isolated from higher rotational levels to be specified as tunnel levels. We notice that the D–H difference in these ammonium compounds is distinct from the normal deuteration effect in a harmonic system represented by malonic acid plotted in Fig. 1.

In Fig. 10, we plot the heat capacities of the normal and deuterated ammonium hexachloroplatinates [27] and hexachloroiridates at low temperatures. Below 27 K, deuterated ammonium hexachloroiridate alone has a large heat capacity, while the other three crystals have the same small heat capacities. This shows that, in the normal ammonium compounds, the rotational levels are at much higher energy than 27 K, while deuterated ammonium hexachloroiridate has extra energy levels comparable

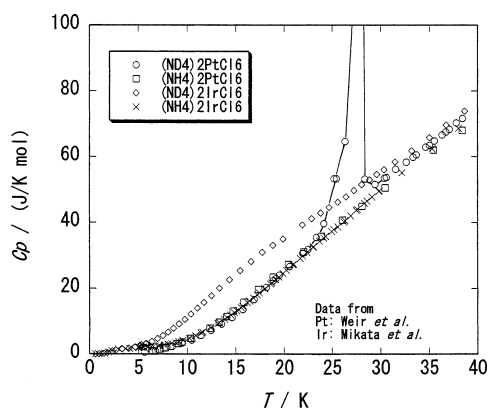


Fig. 10 Low-temperature part of the heat capacity of $(\text{NH}_4)_2\text{PtCl}_6$, $(\text{ND}_4)_2\text{PtCl}_6$, $(\text{NH}_4)_2\text{IrCl}_6$, and $(\text{ND}_4)_2\text{IrCl}_6$. Data from ref. 27 and Mikata *et al.* (to be published).

with 27 K. For deuterated ammonium hexachloroplatinate, the extra energy levels are removed by the first-order phase transition.

NEUTRON DIFFRACTION OF $(\text{NH}_4)_2\text{PtCl}_6$ BY THE STANDARD LEAST-SQUARES ANALYSIS AND BY MAXIMUM ENTROPY METHOD

We performed neutron diffraction on powder samples and single crystals at low temperature. The results obtained by the powder diffraction are shown in Fig. 11 [31]. The Fourier diagrams for $(\text{NH}_4)_2\text{PtCl}_6$ at 6 K, $(\text{NH}_4)_2\text{PtCl}_6$ at 35 K, and $(\text{ND}_4)_2\text{PtCl}_6$ at 35 K all reveal three positions for a proton or deuteron. This result is reasonable and as expected from the heat capacity data for $(\text{ND}_4)_2\text{PtCl}_6$. For $(\text{NH}_4)_2\text{PtCl}_6$ at 6 K, an ordered structure is expected, but the neutron diffraction shows broad distribution of the proton.

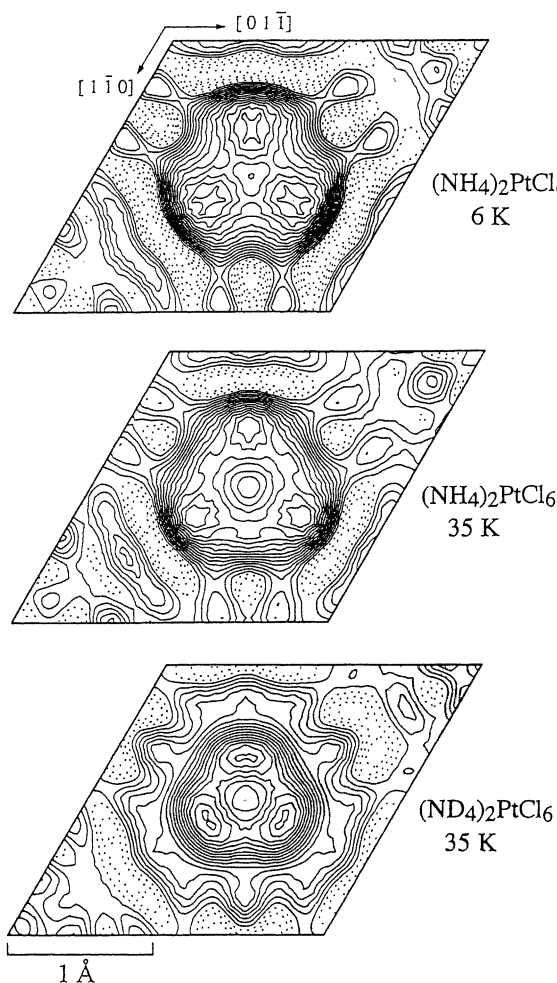


Fig. 11 Fourier maps of the proton and deuteron by powder neutron diffraction [31].

The single-crystal data were collected at 7 K. It is very important that the ammonium ions are essentially in the ground state at this temperature. This is evident from the small value of the heat capacity at 7 K shown in Fig. 10. The neutron data were first analyzed by the standard nonlinear least-squares

method to determine the atomic positions and displacement parameters. It converged to a reasonable structure close to the powder diffraction result. The data were then analyzed by the maximum entropy method. In this method, we divide the unit cell of the crystal into ca. 10 million pixels and assign a density of the neutron-scattering power to each of the pixels. The scattered intensity is calculated for the distribution of the scatterers and compared with the experimental data. If these agree, the assumed distribution is regarded satisfactory. In general, they do not agree. Better agreement between the experimental and calculated scattered intensities is sought using the maximum of the information entropy as the criterion of the good fit, hence, the name “maximum entropy method” (MEM). This gives the least biased interpretation of the experimental data and is suitable for determination of fine details of nuclear distribution. A result of the MEM analysis is given in Fig. 12, showing an ammonium ion in $(\text{NH}_4)_2\text{PtCl}_6$ at 7 K. An extremely interesting point is that the protons are distributed on tori of a ca. 0.08 nm diameter. The enormous size of the distribution is appreciated if we compare it with the nitrogen nucleus located at the center. (The size of the nitrogen nucleus in this figure is determined by the pixel size, and the actual size is still smaller than represented in Fig. 12.)

A diffraction experiment gives the structure averaged in space and time. But in our experiment, all the ammonium ions are essentially in the identical ground state. Therefore, Fig. 12 represents the unique zero point distribution of protons in the crystal. It makes no difference whether or not the image presented in Fig. 12 is a result of space- and time-averaging, because each of the protons, distributed quantum mechanically, should appear the same before and after the averaging. We have thus shown that protons are distributed over a considerable space distance in the ground state. It is appropriate to describe it as a *proton cloud* in analogy with the electron cloud. An interesting question arises here about the phase of the wave function. Since an ammonium ion is rigid, the motion of the four protons in the ion must be correlated, fixing the phase relation among the motion of the four protons. Experiments to detect the effect of this correlation have not been conceived.

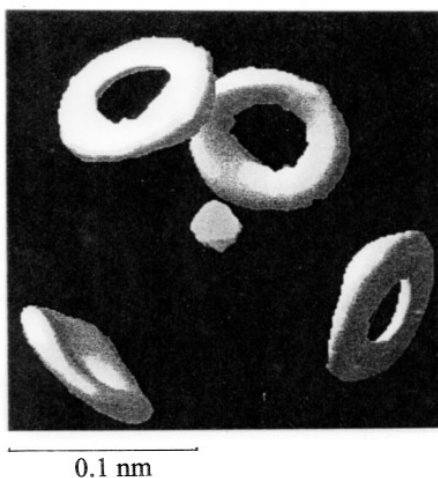


Fig. 12 The MEM reconstruction of the nuclear density of an NH_4 ion in $(\text{NH}_4)_2\text{PtCl}_6$ based on single-crystal neutron diffraction data taken at 7 K.

CHROMIUM OXYHYDROXIDE HCrO_2 AND OXYDEUTEROXIDE DCrO_2

This pair of compounds was studied by X-ray and infrared spectroscopy in 1960 and 1970 [32] and more recently by neutron scattering [33,34]. The interest in this compound is centered on the very short hydrogen bond. Proton tunneling has been assumed [32]. We found a phase transition at 320 K for

DCrO₂ but not for HCrO₂. The heat capacity curves are shown in Fig. 13 [35]. The pronounced peak at 320 K for DCrO₂ and its absence for HCrO₂ is evident. Also, the temperatures of the magnetic anomalies are different (25 K for HCrO₂ and 22 K for DCrO₂).

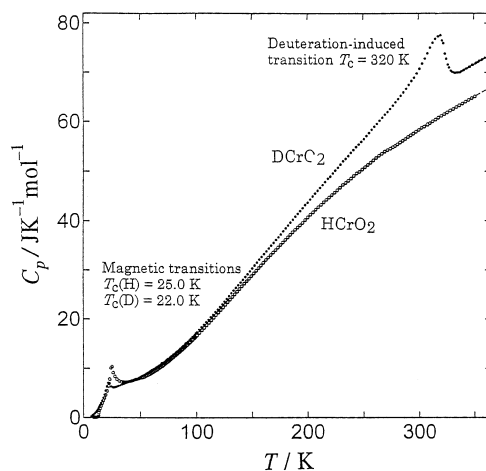


Fig. 13 The heat capacity curves of HCrO₂ and DCrO₂ [35].

The infrared spectra of DCrO₂ are plotted in Fig. 14 for the O–D–O bending mode at temperatures between 5 and 405 K [36]. To take these spectra, the sample was mixed with KBr powder and formed into a disc so that the sample would stay in position in the spectroscopic cell at 5 K as well as 405 K. The phase transition is recognized as a maximum of the bending mode wave number. The corresponding absorption in HCrO₂ occurring at 1200 cm⁻¹ is a smooth function of temperature. We conclude that DCrO₂ undergoes a phase transition at 320 K and that HCrO₂ does not undergo a phase corresponding to this. Far infrared spectra have no peaks below the Cr–O vibration region (ca. 400 cm⁻¹).

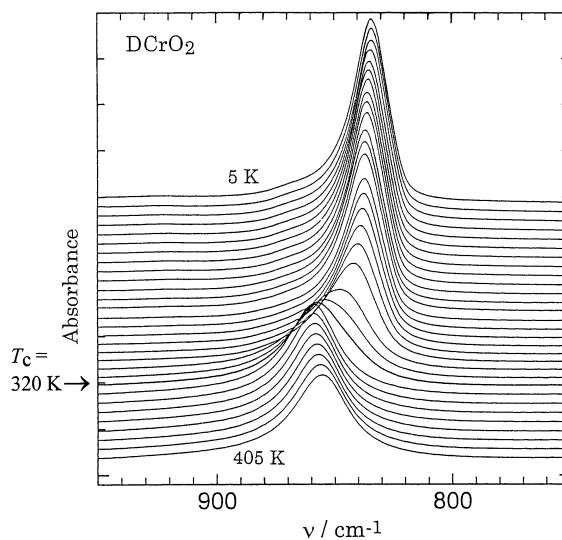


Fig. 14 Temperature dependence of the infrared absorption by the O–D–O bending mode in DCrO₂, showing anomalous behavior at 320 K due to the phase transition [35,36].

Thus, there is no spectroscopically detectable tunneling state in HCrO_2 nor in DCrO_2 . We have shown earlier that the phase transitions in bromodeuteroxy-phenalenone are intimately connected with the tunnel states in bromohydroxyphenalenone. Here, for DCrO_2 , we find a deuteration-induced phase transition, but no tunneling state. It is likely that the isotope mass effect is so drastic in this pair of compound that the hydrogen bond is the single minimum type for HCrO_2 and double minimum type for DCrO_2 . The isotope effect on the hydrogen bond length appears to support this view [33,34].

OTHER COMPOUNDS UNDERGOING DEUTERATION-INDUCED PHASE TRANSITIONS

Sodium deuterioxide undergoes a phase transition at 153 K, but sodium hydroxide does not [37]. The heat capacity of NaOH is larger than that of NaOD at low temperature and suggests the presence of an extra energy level in NaOH . Deuterated diphenyl acetylene also undergoes a deuteration-related phase transition [38]. The transition entropy is small and may be associated with a transition mechanism other than the order–disorder type.

CONCLUSIONS

In the substances discussed here, protons and deuterons move in more or less flat potentials. Their quantum mechanical localization (and delocalization) depends very sensitively on the mass of the particle. This introduces strongly mass-dependent energy levels and is responsible for far infrared absorption and deuteration-induced phase transitions in the hydrogenous and deuterated phenalenone compounds. In some cases [HCrO_2 and probably $\text{A}_3\text{H}(\text{SO}_4)_2$], the potential energy in the hydrogen bond appears to depend strongly on whether there is a proton or deuteron in it. This leads to a shorter hydrogen bond and nonoccurrence of a phase transition in the hydrogenous compound. Neutron diffraction has shown the delocalized wave function of an ammonium ion in the form of a torus of proton cloud. We have shown that such distribution is not a consequence of the space- and time-averaging in the diffraction experiment, but is inherent to the ground state of the ammonium ion.

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