

Spatial Distribution and Tunneling of H and D Atoms in $(\text{NH}_4)_2\text{PtCl}_6$ and $(\text{ND}_4)_2\text{PtCl}_6$ Crystals

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Neutron powder diffraction experiments on $(\text{NH}_4)_2\text{PtCl}_6$ and $(\text{ND}_4)_2\text{PtCl}_6$ have been performed using the time-of-flight high-resolution powder diffractometer *Sirius* at the pulsed cold neutron source in KEK. The Rietveld and Fourier analysis of the data collected at 6 K revealed that the hydrogen atom in $(\text{NH}_4)_2\text{PtCl}_6$ is located about the three-fold axis with three distinct maxima of the distribution function. The result is interpreted in terms of the rotational tunneling of NH_4^+ .

KEYWORDS: neutron powder diffraction, isotope effect, $(\text{NH}_4)_2\text{PtCl}_6$, tunneling

§1. Introduction

$(\text{NH}_4)_2\text{PtCl}_6$ and $(\text{ND}_4)_2\text{PtCl}_6$ belong to a large family of ammonium hexahalometallates $(\text{NH}_4)_2\text{MX}_6$ ($\text{M}=\text{Se}, \text{Pt}, \text{Te}, \text{Pb}, \text{Pd}, \text{X}=\text{Cl}, \text{Br}$) which share the same crystal structure. The basic structure of this compound is of the antiferrotype with NH_4^+ tetrahedra occupying the cation sites at $(1/4, 1/4, 1/4)$ of the fcc unit cell and PtCl_6^{2-} octahedra situated at $(0, 0, 0)$. These compounds undergo novel phase transitions characterized by strong deuterium substitution effects (isotope effects) on the transition temperature (T_{trs}) and the transition entropy ($\Delta_{\text{trs}}S$). The isotope effect depends strongly on the metal and halide atoms. Some undergo a phase transition both in protonated and deuterated forms with a higher T_{trs} and larger $\Delta_{\text{trs}}S$ for the deuterated form,^{1,2)} while others undergo a phase transition only in the deuterated form.³⁻⁸⁾ The magnitudes of $\Delta_{\text{trs}}S$ of the deuterium compounds ($\Delta_{\text{trs}}S > R \ln 2$) suggest that the transitions are of order-disorder type. Interestingly, the symmetry of the cation site ($\bar{4}3m$) coincides with that of an NH_4^+ ion. Therefore, there are no obvious reasons for the cation to be disordered, even though ND_4^+ actually is. For NH_4^+ in those crystals which do not undergo a phase transition to the lowest temperature, the usual argument is that it is not disordered orientationally.

Our recent neutron diffraction study on some deuterated compounds^{9,10)} have showed that the phase transition are due to the orientational ordering of the ND_4^+ ions and that the D atom distribution is quite different for the compounds with strong isotope effect and for those with a weak one. These results indicated that the strong isotope effect is a quantum effects associated with rotational motion of the ammonium ions. However, the

distribution of hydrogen atoms at very low temperature has not been determined. Most of the neutron diffraction experiments have been performed on ND_4^+ compounds so far, because it has been believed that, for NH_4^+ compounds, the incoherent scattering from the H atoms (8 atoms out of 17) would raise the background intensity to a prohibitively high level. Deuterium substitution has been a standard technique of structure determination for substances containing hydrogen atoms. However, since we are interested in the difference in the behavior of protonated and deuterated compounds, we carried out neutron diffraction experiments for $(\text{NH}_4)_2\text{PtCl}_6$ (which undergoes no transition) and $(\text{ND}_4)_2\text{PtCl}_6$ (with $T_{\text{trs}}=27.2$ K). The purpose of the experiment is to make a direct comparison between the spatial distribution of the H and D atoms and then to discuss the mechanism of the strong isotope effect on the phase transition of the $(\text{NH}_4)_2\text{MX}_6$ family. In this paper, we report the result for $(\text{NH}_4)_2\text{PtCl}_6$ obtained at the lowest temperature (6K).

§2. Experiment

Sample crystals were prepared as described elsewhere.¹¹⁾ Neutron diffraction data were collected on the time-of-flight (TOF) high resolution powder diffractometer *Sirius* installed at the pulsed spallation cold neutron source in KEK, Tsukuba, Japan.¹²⁾ The sample crystals [$(\text{NH}_4)_2\text{PtCl}_6$: 4.7756 g, $(\text{ND}_4)_2\text{PtCl}_6$: 5.4938 g] were contained in a vacuum-tight cylindrical can made of vanadium (9 mm in diameter and 60 mm in height) under a helium atmosphere. Intensity data were recorded in the back scattering geometry in the TOF range 7–42 ms, corresponding to the d -spacing range 0.35–2.07 Å. The resolution of the data ($\Delta d/d$) was about 0.1 %.

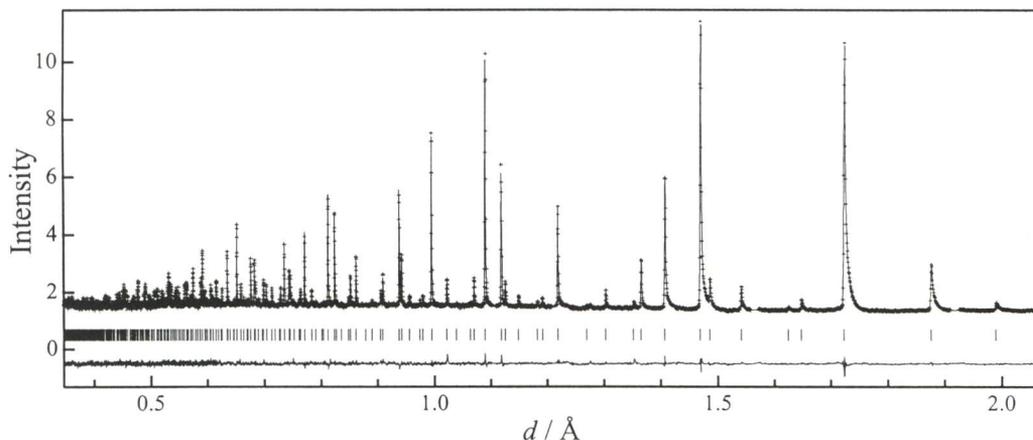


Fig.1. Neutron powder diffraction pattern of $(\text{NH}_4)_2\text{PtCl}_6$ recorded at 6 K. The plus marks denote the observed intensities and the solid line those calculated from the best-fit model of the Rietveld refinement. The tick marks represent the calculated peak positions and the curve below them represents the deviation between observed and calculated intensities.

§3. Results and Discussion

Though the background level of the $(\text{NH}_4)_2\text{PtCl}_6$ data were evidently higher than those of $(\text{ND}_4)_2\text{PtCl}_6$, the statistical quality of the data was good enough for the Rietveld refinement for both of the compounds. Figure 1 shows the powder diffraction pattern of $(\text{NH}_4)_2\text{PtCl}_6$ collected at 6 K. The plus marks denote the observed intensities, and the solid lines those calculated as described below. The observed reflections in the diffraction pattern could be completely indexed with space group $Fm\bar{3}m$.

In the $(1/2 \times 1/2 \times 1/2)$ cube of the $(\text{NH}_4)_2\text{PtCl}_6$ unit cell, the N atom is located at the body center. The NH_4^+ ion is tetrahedrally surrounded by four PtCl_6^{2-} ions with the Pt atom sitting at four corners out of eight. Immediate neighbors of the ammonium ion are twelve chloride ions grouped into four triplets. The four H atoms of the NH_4^+ ion are pointing from the central N atom to the four empty corners (i.e., to the four corners not occupied by Pt atoms). Our recent neutron diffraction study on deuterated compounds has showed that the D atoms are not exactly pointing to the corners on the threefold axes (ordered positions), but are displaced off the threefold axes (disordered positions).^{9,10)}

Distribution of the H atom about the symmetric position on the three-fold axis was explored in detail by the Rietveld analysis. We considered both the ordered and the disordered models for the NH_4^+ ion. In the ordered model, the initial parameters for the heavy atoms are taken from our recent neutron diffraction for $(\text{ND}_4)_2\text{PtCl}_6$ at 35 K.¹⁰⁾ The H atoms in the NH_4^+ ion were placed on the three-fold rotation axis (32f positions, site symmetry: $3m$). The N-H bond length was initially set to 1.0 Å. The 29 variable parameters (15 background parameters, 1 scale factor, 4 profile parameters, 1 lattice constant, 2 atomic coordinates, 6 anisotropic atomic displacement parameters) were refined using 6598 intensity data in the TOF range between 7 - 42 ms ($d = 0.35$ - 2.07 Å). Rapid convergence was obtained to give a χ^2 value of 1.66. The equivalent atomic displacement parameter of the H atom, $B_{\text{eq}}(\text{H}) = 5.9$ Å² was much larger than those

of the other atoms, e.g., $B_{\text{eq}}(\text{N}) = 0.6$ Å². This suggests that the ordered model may be an oversimplification of the actual structure. Therefore, in the next stage of the analysis, refinement on the three-fold disordered model was carried out using additionally one positional and two atomic displacement parameters for the H atom. In this model the H atoms were placed off the three-fold rotational axes and in the mirror planes (96k positions, site symmetry: m). Rapid convergence was obtained again to give a better χ^2 value of 1.61. The calculated intensities from this three-fold disordered model are shown by the solid line in Fig. 1. The tick marks represent the calculated peak positions and the curve below them represents the differences between the observed and calculated intensities.

The distance between the H atom and the three-fold rotation axis is 0.29 Å, corresponding to an NH_4^+ rotation angle of 16.8°. These values are clearly smaller than those in $(\text{ND}_4)_2\text{PtCl}_6$ at 35 K (0.36 Å, 20.9°).¹⁰⁾

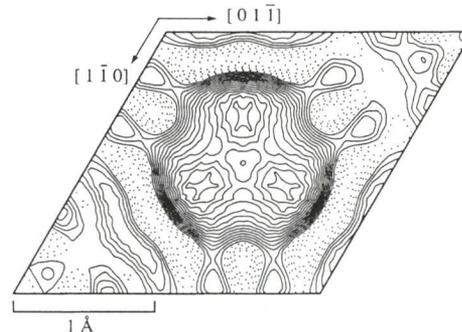


Fig.2. Fourier contour maps (F_{obs}) of the nuclear density in the (111) section at the level containing the H atoms of the NH_4^+ ion. The threefold rotation axis is located at the center of the map.

Figure 2 shows the Fourier contour maps of the (111) section at the level containing the H atom for $(\text{NH}_4)_2\text{PtCl}_6$ at 6 K. The nuclear density was synthesized using the observed structure factors (F_{obs}), lattice

constant in the final structure, and phase data of F_c . For clarity, the sign of the contour lines is reversed to take account of the negative coherent scattering length of hydrogen. The shape of the contour lines changed slightly depending on the data range (high Q limit) used in the synthesis. But the main feature of the distribution remained the same. The map clearly shows that H atoms are located about three maximum positions in the mirror planes and away from the threefold axis; the position on the three fold axis is a local minimum of the density. $(ND_4)_2PtCl_6$ undergoes an order-disorder type phase transition at 27 K. Below this temperature, the orientation of the ND_4^+ ion is ordered in the low temperature structure. In contrast, $(NH_4)_2PtCl_6$ remains in the same cubic phase down to 6 K. It is unlikely that a phase transition occurs below 6 K. We have shown in the above that the hydrogen atom is delocalized over a region of space about the three-fold axis. We emphasize that the data were collected at low temperature (6 K). In view of the phase transition temperatures of various ammonium compounds (mostly 100-300 K), the temperature 6 K is low enough to guarantee that the structure is essentially that of the crystal at zero kelvin. This excludes the possibility that the observed three-fold distribution resulted from superposition of orientationally disordered NH_4^+ ions. With this in mind, we conclude that the orientational ground state is a tunneling state formed by a symmetrical combination of the localized states in the space of rotational angles of an ammonium ion. Finally we point out that rigid body rotation of an ammonium ion about the N atom fixed at the $\bar{4}3m$ position produces six equivalent positions resulting from positive and negative rotations about three axes (x , y

and z). Thus the three maxima of the distribution of the proton density are not consistent with the rigid body rotation. But these are reconciled with each other if the three maxima are actually the six maxima closely paired into three. In fact we tried the six-fold model in which the H atoms were placed at the $192l$ sites (general positions) with site occupancy of 1/6, but the fitting did not improved any more. Detailed description of the tunneling states is still to be worked out.

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- 1) Y. Kume, H. Muraoka, T. Matsuo and H. Suga : J. Chem. Thermodyn. **26** (1994) 211.
 - 2) J. E. Callanan, R.D.Weir and E. F. Westrum, Jr : J. Chem. Thermodyn. **27** (1995) 299.
 - 3) R. D. Weir and E. F. Westrum, Jr : J. Chem. Thermodyn. **22** (1990) 1097.
 - 4) R. D. Weir and E. F. Westrum, Jr : J. Chem. Thermodyn. **23** (1990) 653.
 - 5) J. E. Callanan, R. D. Weir and E. F. Westrum, Jr : J. Chem. Thermodyn. **24** (1992) 1001.
 - 6) J. E. Callanan, R. D. Weir and E. F. Westrum, Jr : Ber. Bunsenges. Phys.Chem. **96** (1992) 1585.
 - 7) H. Muraoka, T. Matsuo and Y. Kume : Solid State Commun. **93** (1995) 529.
 - 8) Y. Kume, Y. Miyazaki, T. Matsuo and H. Suga : J. Phys. Chem. Solids **53** (1992) 1297.
 - 9) O. Yamamuro, H. Muraoka, T. Ohta, T. Matsuo, Y. Kume, N. Onoda-Yamamuro, K. Oikawa and T. Kamiyama : J. Phys. Soc. Jpn. **64** (1995) 2722.
 - 10) O. Yamamuro, K. Okishiro, T. Matsuo, N. Onoda-Yamamuro, K. Oikawa, T. Kamiyama, Y. Kume and F. Izumi : J. Chem. Phys. **107** (1997) 8004.
 - 11) Y. Kume and T. Asaji : J. Mol. Structure **345** (1995) 145.
 - 12) S. Torii, T. Kamiyama, K. Mori, K. Oikawa, S. Itoh, M. Furusaka, S. Satoh, S. Ikeda, F. Izumi and H. Asano : J. Phys. Chem. Solids **60** (1999) 1583.