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Importance of water content and motion in the one-dimensional conductor $K_2Pt(CN)_4Cl_{0.3} \cdot n\,H_2O$

M. A. Butler and H. J. Guggenheim
Bell Laboratories, Murray Hill, New Jersey 07974

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The proton NMR has been examined as a function of temperature in $K_2Pt(CN)_4Cl_{0.3} \cdot n\,H_2O$. Our results indicate a distribution of tumbling times for the water molecules. This is explained in terms of the interaction of the permanent electric dipole moment of the water with a distribution of electric fields in the crystal caused by a random occupation of the K^+ and Cl sites. It is proposed that the importance of the waters of hydration to this class of materials arises from their electric dipole moments. In particular we feel that the ordering of these moments provides significant shielding of the platinum chains from the potentials generated by the random occupation of the K^+ and Cl^- sites. This provides a natural explanation for the dependence of conductivity on water content.

INTRODUCTION

Recent studies of the square planar platinum-cyanide complexes as examples of one-dimensional conductors have made people aware of the important role that the waters of hydration play in these compounds.[1–3] The physical properties of these materials vary drastically with water content, and the crystals will crumble to a grey powder if they are completely dehydrated.[1] Thus water is quite important and yet it is very loosely bound as it may be removed by exposing the samples to vacuum. Therefore we wish to determine the nature of the role played by the water molecules. Specifically, is the water important because it fills the holes in the crystals and thus provides structural support, or because of some particular physical property of water molecules?

As a means of approaching this problem we have examined the proton NMR in powdered samples of $K_2Pt(CN)_4Cl_{0.3} \cdot nH_2O$ ($n = 2.6$) as a function of temperature. These measurements indicate that some of the water molecules are free to rotate in such a manner as to narrow the resonance and that this motion freezes out at temperatures below ~ 200 °K. This behavior is very reminiscent of molecules adsorbed on surfaces or into channels and thus we will use the theories developed to interpret these experiments[4] to also interpret our data.

Based on these theories the temperature dependence of the NMR suggests a distribution of molecular tumbling times for the H_2O molecule. We postulate that such a distribution can arise if the tumbling is an activated process and the activation energy comes from the interaction of the electric-dipole moment of the H_2O molecule with the local electric fields. A distribution of such fields would be caused by the nonregular occupation of the K^+ and Cl^- sites. This idea is then explored further by a simple zeroth-order calculation of such fields at the H_2O sites.

With the NMR results pointing to the importance of the electric-dipole moments of the H_2O molecules, we then consider the effect that they might play in the conductivity of these materials. In particular we feel that the ordering of these moments provides significant shielding of the Pt chains from the potentials generated by the disorder in these crystals. This provides a natural explanation for the dependence of conductivity on water content.

EXPERIMENTAL PROCEDURE

The compounds $K_2Pt(CN)_4X_{0.3} \cdot nH_2O$, where X is a halogen ion, are known to be isostructural and have the structure shown in Fig. 1.[5] The unusual one-dimensional character of these compounds is clearly due to the platinum atoms forming chains along the c axis with a spacing (2.88 Å), comparable to that in metallic platinum (2.78 Å). The accepted picture of conduction is that the Pt($5d_{z^2}$) orbitals overlap to form a band and that the halogen ions act as acceptors removing electrons to make the band $\frac{5}{6}$ filled. This simple picture is complicated by the sensitivity of one-dimensional systems to breaks in the chains,[6] Peierl's distortions,[7] and disorder.[8] Rather than indulge in arguments over which of these effects dominates the conduction process, we wish to consider only the contribution that the water molecules might make. For our interpretation of these effects, it is important to note that only half of the available K^+ sites and $\frac{2}{3}$ of the halogen sites are occupied, presumably in a random manner. Since there are six water sites per unit cell, a fully hydrated crystal should have $n = 3$ in the chemical formula. Notice that there are basically two types of sites for the H_2O molecules both of which are relatively close to the K^+ and Cl^- sites.

Our samples were prepared by reacting high-purity platinum metal with aqua regia until all

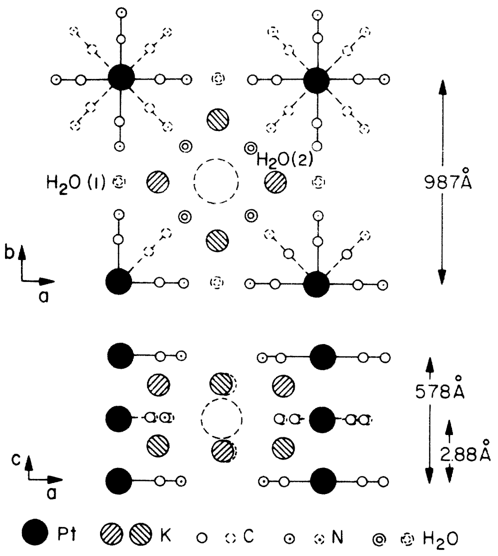

FIG. 1. Structure of $K_2Pt(CN)_4X_{0.3}\cdot nH_2O$ as determined by Krogmann and Hausen (Ref. 5). Note that the platinum atoms form chains along the c axis with a spacing comparable to that in metallic platinum. The large space at the center of the unit cell is occupied $\frac{2}{3}$ of the time by the halogen ion. Similarly only $\frac{1}{2}$ of the K^+ sites are occupied. The distribution of these appears random. The two types of water sites are labeled for future reference.

dissolved and then evaporating to dryness. This procedure produces H_2PtCl_6 which is subsequently heated to 350 °C in N_2 to yield $PtCl_2$. The dichloride is then reacted with a four molar aqueous solution of potassium cyanide with the following reaction taking place:

$$PtCl_2 + 4KCN \rightarrow K_2[Pt(CN)_4]\cdot 3H_2O + 2KCl. \tag{1}$$

The removal of the heavy concentration of KCl was best accomplished by repeated fractional crystallizations. For the preparation of the partially oxidized compounds,[5] a portion of the pure compound was chlorinated in solution to saturation and then mixed with the unchlorinated solution in the ratio 1:5. Because of the lower solubility of the partially oxidized compound it is the first phase to precipitate. The particular samples used in these experiments were found to have 5.2 H_2O molecules per unit cell as determined by thermogravimetric techniques.

The proton NMR was observed using a simple bridge spectrometer[9] operated at ~40 MHz with a 12-in. Varian magnet providing the field. Temperature control was by a helium gas-flow system. A typical spectrum is shown in Fig. 2.

NMR RESULTS

In order to interpret our NMR data let us first consider what type of spectrum is expected for waters of hydration. For a rigid water molecule in a magnetic field H_0 the Hamiltonian is given by[10]

$$\mathcal{H} = -\gamma\hbar H_0(I_1^z + I_2^z) + (\gamma^2\hbar^2/r^3) \times [\vec{I}_1\cdot\vec{I}_2 - 3(\vec{I}_1\cdot\hat{n})(\vec{I}_2\cdot\hat{n})], \tag{2}$$

where I_1 and I_2 identify the two protons, γ is the gyromagnetic ratio, r the separation between the two protons, and $\hat{n}$ a unit vector along r. Since we are interested in the limit where the Zeeman term dominates, perturbation theory may be used to obtain the resonance frequencies[10]:

$$\nu = \gamma H_0 \pm \tfrac{3}{4}(\gamma^2 h/r^3)(3\cos^2\theta - 1), \tag{3}$$

where θ is the angle between $\hat{n}$ and H_0. Because our experiments were done at a fixed frequency with a varying field, the spectrum is given by[10]

$$H_0 = \nu/\gamma \pm \tfrac{3}{4}(\gamma h/r^3)(3\cos^2\theta - 1). \tag{4}$$

Thus for a single crystal the spectrum would consist of a doublet whose splitting varies as the crystal is rotated. Such measurements on a single crystal of $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$ have been made at room temperature by Brugger and Brinkmann.[11] They observed three doublets, two with the splitting expected for waters of hydration and one with one quarter of that splitting. The two doublets with "normal" splittings were attributed to the $H_2O(2)$ sites (see Fig. 1) and the narrowed doublet to the $H_2O(1)$ site with the molecule exhibiting the

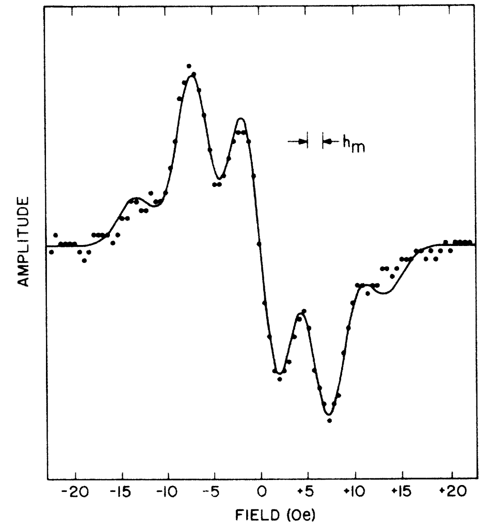

FIG. 2. Proton NMR in $K_2Pt(CN)_4Cl_{0.3}\cdot 2.6\,H_2O$ at 40.3 MHz and 227 °K. The points result from manually digitizing the data while the curve is a least-squares fit to the data using a model discussed in the text. The modulation amplitude h_m is also indicated.

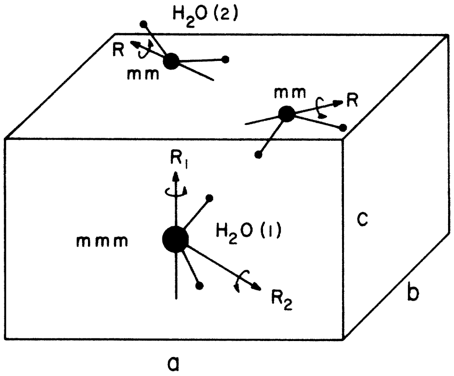

FIG. 3. Orientations of the rotation vectors for the two kinds of the sites in $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$ from Ref. 11. The two possibilities for the $H_2O(2)$ sites are not distinguishable using the NMR results!

rotations shown in Fig. 3. The combination of these two rotations provide the necessary motion to narrow the doublet to $\frac{1}{4}$ its original splitting by averaging $\cos^2\theta$ over these motions.[12] The rotations shown for the $H_2O(2)$ sites are not detectable by the NMR because they do not change $\cos^2\theta$. These rotations are included by Brugger and Brinkmann so that the H_2O molecules have the proper symmetry to fit the point symmetry of the site.

With these single-crystal measurements having been performed, one might ask what additional information may be learned from the powder experiments we have performed. Actually our interests center on the temperature dependence of H^1 NMR but the single-crystal results have been presented because they provide guidance in understanding our spectra and because our results will shed some light on the single-crystal results. Based on Brugger and Brinkmann's work, the outer lines of our spectrum in Fig. 2 can be identified with the $H_2O(2)$ sites and the central component with the motionally narrowed $H_2O(1)$ site.

As the temperature is varied the qualitative features of the spectrum are that the relative intensities of the central and outer lines change but that the width of these lines does not change. This is rather unusual, as one normally expects that as molecular motion slows down the narrowed resonance will first broaden and smear out before forming the doublet spectrum expected with no motion.[10]

The behavior observed in our samples has been observed previously for molecules that are adsorbed onto surfaces or into channels in other materials. Examples are water and benzene adsorbed on charcoal[4,13] and water adsorbed into zeolite.[14] The explanation of the NMR behavior in these examples is that there are a large number of slightly different sites which for a given temperature result in a distribution of tumbling times.[15] This is illustrated in Fig. 4. Only those molecules whose tumbling times are close to τ_c (indicated by the cross-hatched area), the critical value which separates the spectra which will be narrowed and those which will appear to have no motion, will result in a smeared out spectrum. Those sites with tumbling times much longer will have a well-defined stationary spectrum and those much shorter will have a narrowed spectrum. Therefore, as long as the cross-hatched area represents a small fraction of the molecules, the smearing out of the spectra will not be noticed. As the temperature changes, the distribution of tumbling times will sweep past τ_c giving the type of spectra we are observing.

All of this behavior has been treated quantitatively[4] and in order to use these results our spectra must first be fit to obtain the necessary parameters. The normal powder pattern for waters of hydration is shown in Fig. 5. This must then be convoluted with a line-shape function which for dipolar interactions is normally taken to be Gaussian.[9] The resulting function is not analytic and thus difficult and expensive to use in a least-squares fitting procedure. To simplify matters the powder pattern has been approximated by the spectrum shown as a dashed line in Fig. 5. Convoluting this approximation with a Gaussian line shape results in a function amenable to our fitting procedures. The derivative of this function is fit to both the central component and the outer lines of our spectrum by a least-squares fitting procedure. A typical fit is shown in Fig. 2. The results of fitting the data indeed show that the rela-

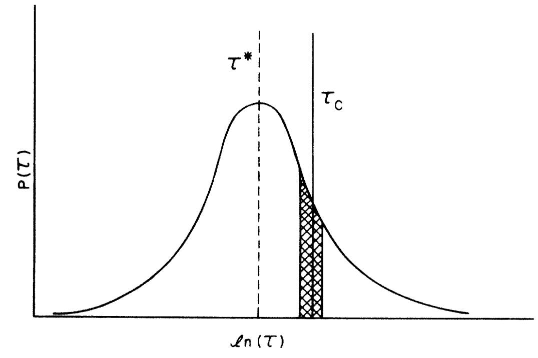

FIG. 4. Hypothetical distribution in tumbling times for adsorbed molecules. Notice that the distribution function is plotted vs $\ln\tau$. This is to emphasize that the tumbling is an activated process and the distribution arises from a distribution in activation energies. τ_c is the critical time which separates the molecules which contribute to the motionally narrowed and stationary NMR spectra. The cross-hatched area results in a smeared spectrum. τ^* is the median of the distribution.

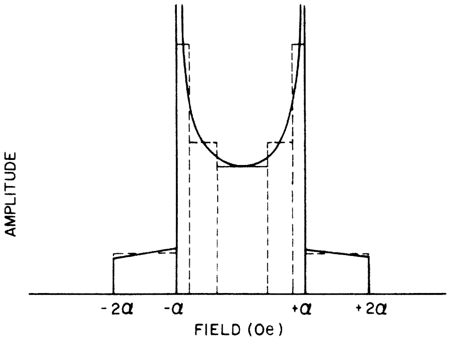

FIG. 5. Solid line is the expected powder pattern for waters of hydration with $\alpha = 3\gamma h/4r^3$. The dashed line is the model spectrum we used to fit our data.

tive intensities of the two peaks change while their widths remain constant. A plot of the fraction of molecules contributing to the central component f_m is shown in Fig. 6.

A question that is immediately raised by these results is why f_m should go above 0.33. If the crystal is fully hydrated and only the $H_2O(1)$ site contributes to the central component, f_m would not be expected to go above 0.33. However, as our samples are not fully hydrated ($n = 2.6$) and if the dehydration process preferentially removes water from the $H_2O(2)$ sites, it would be possible to get an f_m above 0.33. This interpretation is supported by one case in which we accidentally overheated the sample driving off some water. Afterwards an f_m of 0.56 at 280 °K was measured, considerably above the number for our nominal samples. It should be remembered that the ease with which molecules rotate is not necessarily an indication of the ease with which they may be removed from the crystal. That it is easier to remove the water in the $H_2O(2)$ sites is also suggested by the crystal structure. These sites are closer to the center of the unit cell which consists of a quite open structure because of the partial occupation of the K^+ and Cl^- sites.

APPARENT PHASE-CHANGE MODEL

In order to explain the behavior of f_m we now turn to a quantitative model constructed by Resing[4] which shows how a distribution in tumbling times affects the NMR line shapes and relaxation times of adsorbed molecules. It will be assumed that the tumbling is an activated process with

$$\tau = \tau_0 e^{E/kT}, \qquad (5)$$

where τ_0 is a characteristic time and E the activation energy. In which case a Gaussian distribution in E would give a Gaussian distribution in $\ln\tau$. For this reason the distribution function is taken to have the form

$$P(\tau)\, d\tau = (B/\pi^{1/2})\, e^{-B^2 Z^2}\, dZ\ , \qquad (6)$$

where $Z = \ln(\tau/\tau^*)$, τ^* is the median of the distribution, and $B = (1/\sqrt{2})\,\sigma_Z$ with σ_Z one standard deviation in the Z distribution. The fraction of nuclei contributing to the central component of the line is then given by integrating $P(\tau)$ from $\tau = 0$ to τ_c. This may be expressed as

$$f_m = (1/\pi^{1/2}) \int_{-\infty}^{\nu_c} e^{-x^2}\, dx, \qquad (7)$$

where $\nu_c = BZ_c$ and $Z_c = \ln(\tau_c/\tau^*)$. For our system the critical tumbling time is defined by $\gamma \Delta H \tau_c = 1$, where ΔH is the splitting of the doublet for the $H_2O(2)$ sites. Thus we can use Eq. (7) to fit the experimental f_m data given in Fig. 6. The fully hydrated crystals require the parameters given by $\nu_c = aT - b$, where $a = (1/\sqrt{2}\,\sigma_E)\ln(\tau_c/\tau_0)$, $b = (E^*/\sqrt{2}\,\sigma_E)$, σ_E is one standard deviation of the energy distribution, and E^* is the median activation energy. You will notice that E^*, σ_E, and τ_0 cannot be independently determined; only relations between these parameters. Using a and b as adjustable parameters, the experimental data have been fit for $f_m(\max) = 0.39$ which corresponds to $n = 2.6$ with the water loss coming only from the $H_2O(2)$ sites. Assuming the water loss is equally from both water sites or preferentially from the $H_2O(1)$ site will result in a smaller $f_m(\max)$ and thus worse fits to the data. The resulting parameters for the fit are shown in Fig. 6. Keep in mind that this model assumes a Gaussian distribu-

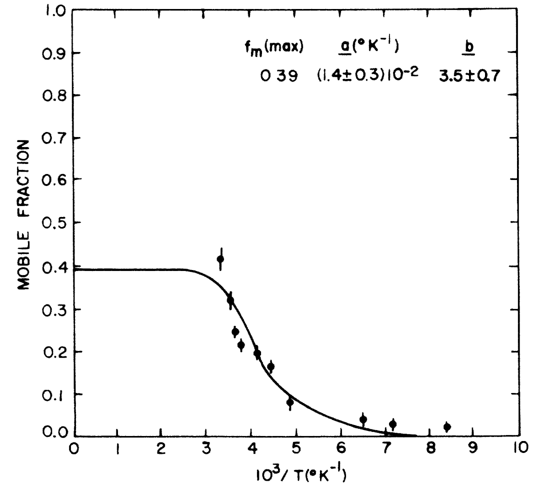

FIG. 6. Fraction of nuclei that are tumbling (contributing to the central component of the resonance) as a function of temperature. The line is a least-square fit to the data using the apparent phase-change model discussed in the text. The parameters determined from this fit are also shown.

tion in activation energies which may or may not be reasonable in the one-dimensional platinum salts.

It thus appears that the temperature dependence of the NMR data can be satisfactorily explained using the apparent phase-change model. We are then in a position to ask what is the origin of the distribution in activation energies for the tumbling of the water molecules?

ELECTRIC-DIPOLE INTERACTION

The only feature of these materials which offers a ready explanation to the above question is the "random" occupation of the K^+ and Cl^- sites. We propose that the activation energy for tumbling of the H_2O molecules is a result of the interaction of the H_2O electric-dipole moment p with the local electric fields. The distribution of activation energies comes about from the distribution in electric fields caused by the irregular occupancy of the K^+ and Cl^- sites.

To examine this idea in somewhat more detail, we have calculated the electric fields at the two water sites using a simple model in which there is *no* randomness. This was done by using the appropriate fractional charges in each site such that the unit cell as a whole is completely neutral. Sites within a unit cell had their average charge while sites shared between two or more unit cells were given their average charge divided by the number of unit cells sharing the site. Thus the Cl^- site had a charge of $-\frac{2}{3}$, the K^+ sites had a charge of $+\frac{1}{2}$, the C and N sites had a charge of either $-\frac{1}{2}$ or $-\frac{1}{8}$, and the Pt site had a charge of $+\frac{7}{12}$ or $+\frac{7}{24}$. The water molecule was considered a neutral entity and thus ignored. This zeroth-order model is an over simplification because there is no disorder and thus no distribution in electric fields at the H_2O sites. Furthermore, it neglects the dipolar field of the water molecules which could be a significant contribution.

Using this distribution we then summed over lattice sites to obtain the electric field at each water molecule site. If you examine Fig. 1 it is apparent that the electric fields at the $H_2O(1)$ sites should be identically zero because this is a point of inversion symmetry. Thus for every charge at a point r there is an identical charge at the point $-r$, and the sum of all these electric fields at the $H_2O(1)$ site will be zero. The $H_2O(2)$ site is not a point of inversion symmetry and summing over lattice sites we find an electric field of ~ 1 V/Å pointing diagonally from the center of the unit cell to the corner. Such a field would give an activation energy pE of $\sim 4500\,^\circ$K. An activation energy this large would preclude the rotation of water molecules in the $H_2O(2)$ sites. The electric field we have calculated would require the dipole moment to align along the unit cell diagonal thus deciding between the two orientations proposed by Brugger and Brinkmann. The inclusion of the interaction between dipole moment and electric field would also make the rotations at the $H_2O(2)$ site indicated in Fig. 3 unnecessary. It appears then that our simple model accounts for the rigidity of water in one site and its freedom in the other. Extension of the model to include disorder would be difficult as the distribution of K^+ and Cl^- ions would not be completely random. It appears that local charge neutrality would play a significant role. However, if the distribution of the ions is ever determined, NMR will provide a convenient check as the $H_2O(1)$ site directly reflects the disorder.

CONDUCTIVITY

The interaction of the electric-dipole moment of the water molecules with the local fields in the crystal can have important implication for other physical properties of these materials. In particular we would like to consider the role that this interaction might play in the conductivity. It is an experimental fact that water content drastically affects the conductivity. However, the Peierls transition,[7] which is believed to be the dominant factor in determining the conductivity, by itself does not provide an explanation for this effect. We believe that this comes about in the following manner. The orientation of the water electric-dipole moment in the local fields will provide some shielding of the platinum chains from the random potentials generated by the irregular occupancy of the K^+ and Cl^- sites. Since a spatially varying potential along the platinum chains provides a scattering mechanism for the electrons, we expect the removal of some water to increase the "random" potential and thus lower the conductivity. The actual response of the system is probably more complicated than this since the disorder is expected to affect the Peierls transition.[16] Under some circumstances this may result in an increased rather than decreased conductivity. However, the mechanism we propose provides the interaction between the H_2O molecules and the conduction electrons which is necessary to explain the observed strong dependence of conductivity on water content.

CONCLUSIONS

We have shown that the temperature dependence of the proton NMR in the one-dimensional platinum salts can be explained by a distribution of activation energies for molecular rotation. It is proposed that these activation energies are determined by the interaction of the water-molecule electric-dipole moment with the local electric fields in the crystal. The distribution in such fields would then arise from the irregular occupancy of the K^+ and Cl^- sites. A simple calculation of such local fields explains why only H_2O molecules in one site are free to rotate and distinguishes between the two possible molecular orientations proposed by Brugger and Brinkmann[11] for the nonrotating site. Furthermore, we have examined the effects of the water molecules on conduction in these materials. It is proposed that the water molecules provide a shielding mechanism to protect the platinum chains from the sizeable random potentials. This provides a natural explanation of why loss of water results in a drop in conductivity and under severe circumstances can destroy the crystal.

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