

Motion of interlamellar hydrated sodium ions in layered $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$

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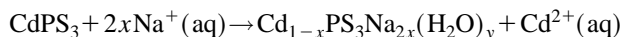
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The motion of hydrated Na ions in the galleries of layered $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ have been investigated by proton and ^{23}Na NMR and impedance measurements as a function of temperature. The material is conducting and the frequency dependent conductivity exhibits a power law characteristic of non-Debye-like electrical conductivity relaxation, arising from Coulomb correlation among charge carriers. The NMR spectra indicates that the interlamellar Na ions are mobile and there is good agreement between the ^{23}Na spin-lattice relaxation rates and the electrical conductivity relaxation. The proton NMR exhibits a well resolved orientation dependent dipolar splitting which has been rationalized by considering the anisotropic rotational motion of water molecules in the pseudo-octahedral hydration shell of the Na ion. Isotropically tumbling water as well as proton hopping among water molecules is absent in $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$. Evidence is presented to show that within the galleries the Na ion moves along with its hydration shell, the motion being such that the orientation of the \vec{C}_2 axis of the water molecule with respect to the normal to the layers is always preserved. The motion of the hydrated Na ions are correlated through their mutual Coulombic interaction but the rotational motion of the water molecule in the ions hydration shell may still be described by a single exponential Debye-like relaxation.

I. INTRODUCTION

The layered cadmium thiophosphate, CdPS_3 undergoes an unusual ion-exchange intercalation reaction in which hydrated alkali cations from an aqueous solution insert into the interlamellar space with an equivalent loss of cadmium ions, leaving immobile vacancies in the layer.¹ The host lattice, cadmium thiophosphate, is formed by the stacking of CdPS_3 sheets, built from edge sharing CdS_6 and P_2S_6 polyhedra. The van der Waals gap is 3.2 Å.² Intercalation occurs with a dilation of the lattice along the interlayer axis, the extent of which depends on the nature of the guest cation and the extent of its hydration. The intercalation reaction may be written as



$$x = 0.25, \quad y = 2$$

where the guest species, hydrated Na ions, reside in the interlamellar space. The lattice expansion on intercalation, Δd , is 5.6 Å; this is twice the van der Waals diameter of a water molecule. The projected electron density as calculated from the x-ray diffraction 00 l peaks show that the water molecules in the galleries form a bilayer with Na ions located in the center of the gap.³ In conjunction with the lattice expansion this suggests that the Na ions are probably located in the octahedral interstices of the H_2O bilayer (Fig. 1). The octahedral hydration shell for the Na ion would be similar to that

proposed for the interlamellar hydrated ions in mica type silicates.⁴ The density of the interlamellar water, as calculated from the stoichiometry and lattice parameters, indicates that the two dimensional bilayer is not infinite but broken up into islands or clusters. Alternatively these clusters may be viewed as being formed by edge sharing $\text{Na}(\text{H}_2\text{O})_6$ octahedra. This model accounts not only for the density of the interlamellar water but also the average Na to H_2O stoichiometric ratio of 1:4 which is in between that of an isolated $\text{Na}(\text{H}_2\text{O})_6$ and the infinite $\text{Na}(\text{H}_2\text{O})_2$ sheet. $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ is conducting with a dc conductivity of 10^{-6} s/cm at 300 K and Arrhenius activation energy 15.6 kcal/mol.⁵ In these compounds the negatively charged $\text{Cd}_{0.75}\text{PS}_3$ sheets are electrically inert and the conductivity is due entirely to the interlamellar hydrated ions.^{3,5} In this paper we report the results of our study on the motion of H_2O molecules and Na ions confined in the galleries of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ by ^1H and ^{23}Na NMR spectroscopy in conjunction with frequency-dependent impedance measurements. This system is particularly attractive since it may be effectively modeled as hydrated alkali ions confined between two uniformly charged insulating sheets.

Line shape analysis and relaxation measurements in NMR spectra have been widely used to investigate molecular motion. The line shape provides direct evidence of nuclear couplings that depend on the relative positions of the nuclei. In the presence of rapid, isotropic motion position and orientation dependent nuclear-spin interactions are averaged to zero. However, in samples where molecules undergo anisotropic motions the NMR spectra can exhibit structures due to

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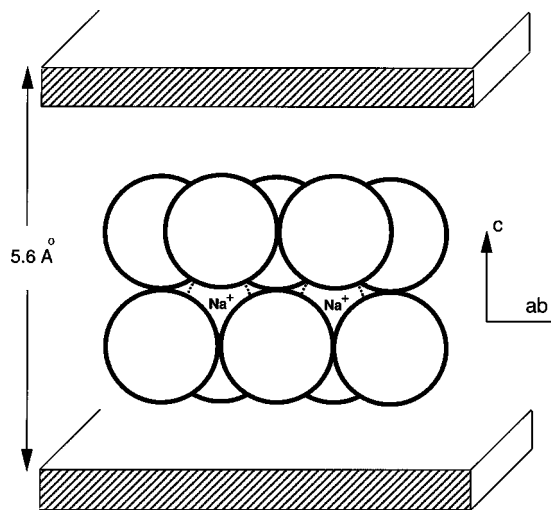


FIG. 1. The bilayer arrangement of water molecules in the galleries of layered $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$. The Na ions occupy the octahedral voids.

an incomplete averaging of the nuclear-spin interactions. The NMR spectra in such situations provide a probe for the dynamics and type of motion of the nuclear spins. The technique has been used to study the motion of guest molecules intercalated in layered host lattices.⁶ Motion of the guest in such systems has been shown to be strongly anisotropic due to the constrained environment imposed by the host lattice layers. There have been previous reports on ^1H NMR of hydrated layered compounds especially clays⁷ and the layered hydrated chalcogenides.⁸ In most of these compounds the proton NMR displays a nearly classical Pake line shape as calculated for a two proton dipole-dipole interaction. This feature had been assigned to water molecules undergoing anisotropic two dimensional diffusion while an additional narrow central line in the ^1H spectra to water molecule undergoing isotropic tumbling and/or proton exchange.

In compounds which exhibit ionic conductivity, NMR in combination with electrical conductivity measurements can provide information on the nature and dynamics of the transport process. Frequency-dependent conductivity measurements have been widely used to explore correlation effects among charge carriers. The close relation between the electrical conductivity relaxation (ECR) derived from the complex impedance and the nuclear spin lattice relaxation (SLR) have been pointed out by various workers.⁹⁻¹¹ The correlation function describing ECR and SLR in ionic conductors usually show a similar deviation from single exponential decay characteristic of Bloembergen-Purcell-Pound (BPP) or ideal Debye-like relaxation.¹²

II. EXPERIMENT

Cadmium thiophosphate, CdPS_3 , was prepared from the elements following the procedure reported in Ref. 13. Platelet-like crystals of CdPS_3 were grown by chemical vapor transport using sulfur as a transporting agent. Powder as well as crystals of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ were prepared by stirring CdPS_3 with 1 M aqueous solution of NaCl in the presence of EDTA.³ $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{D}_2\text{O})_2$ was prepared by a similar procedure with the appropriate solutions made in

D_2O . The formation of the intercalated compound was confirmed by powder x-ray diffraction (Shimadzu XD-D1; $\text{Cu-K}\alpha$). Cadmium and sodium ion stoichiometries were established by atomic absorption spectrometry (AAS) and the extent of hydration by thermogravimetric measurements. Static ^1H and ^{23}Na spectra of the powder and single crystal samples of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ were recorded on a Bruker DSX-300 solid state FT-NMR spectrometer at Larmor frequencies of 300.13 and 79.35 MHz, respectively. Static ^2H NMR spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{D}_2\text{O})_2$ powder was also recorded, at a Larmor frequency of 46.07 MHz. All the (^1H , ^{23}Na , and ^2H) spectra were obtained by a Fourier transform of the free induction decay (FID) following a single $\pi/2$ pulse. Temperature variation studies on both single crystal and powder samples were done using the Bruker temperature accessory (B-VT 2000). Angular variation of the crystal spectra was studied using an assembly similar to that in Ref. 14. The ^1H and ^{23}Na spin-lattice relaxation times at various temperatures were determined by sampling the free induction decays (FID) following the $\pi/2$ pulse in the $\pi - \tau - \pi/2$ “inversion-recovery” sequence followed by Fourier transform of the FIDs for about 12 values of τ .

Electrical measurements were made on pelletized samples using platinum electrodes. Sample temperature could be varied from 30 to 250 K with ± 0.5 K accuracy using a closed cycle cryostat (CTI-cryogenics). The complex admittance, $Y^* = Y' + iY''$, was measured in the frequency range $10 - 10^5$ Hz using a dual phase lock-in analyzer (PAR 5208).¹⁵ The physical quantities of interest, the real and imaginary parts of the complex dielectric permittivity and the complex electrical modulus,¹⁶ M^* , which is the reciprocal of the complex dielectric permittivity, ϵ^* , were derived from the complex admittance, Y^* . $\epsilon^* = Y^*/i\omega C_0$ where C_0 is the vacuum capacitance of the cell, $C_0 = \epsilon_0 A/d$. A is the area of the electrode, d is the thickness of the sample, and $\epsilon_0 = 8.854 \times 10^{-12}$ F/m. The conductivity measurements were limited to 250 K since above this temperature there was partial loss of water from $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ due to evacuation of the cryostat.

III. RESULTS AND DISCUSSION

A. ^1H NMR spectroscopy

The ^1H powder NMR spectrum of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ shows a well resolved Pake powder pattern¹⁷ at room temperature (Fig. 2), characteristic of an isolated, dipolar-coupled pair of spins. The separation between the singularities and the shoulders are 6.7 and 13.4 kHz, respectively. The ^1H NMR spectra of oriented crystals of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ were recorded as a function of the angle δ between C^* , the vector normal to the layers, and the external magnetic field, H_o . At all angles a pair of lines was obtained. The angular variation of the doublet separation, Δ , is shown in Fig. 3, and follows $\Delta = 13(3 \cos^2 \delta - 1)/2$. The temperature variation of the ^1H NMR spectra of crystals of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ for $\delta = 0^\circ$ is shown in Fig. 4. The most striking feature is that the doublet separation, 13 kHz, shows no change with temperature; the only temperature dependent feature is the linewidth of the individual components, which

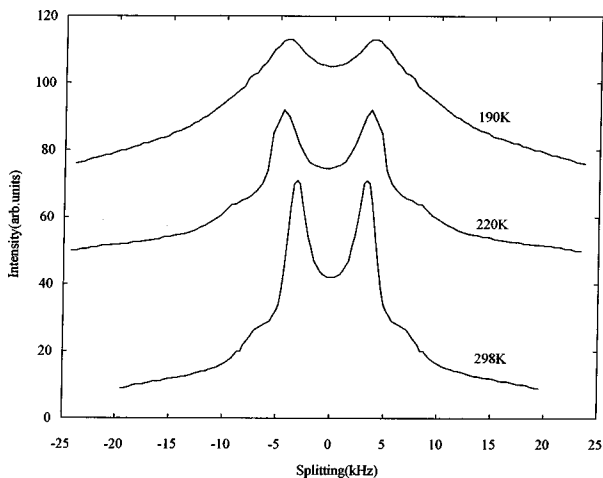


FIG. 2. ^1H NMR spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ powder at various temperatures.

narrows from a full width at half maxima (FWHM) of 2850 Hz at 230 K to 800 Hz at 295 K (Fig. 4) (spectra were not recorded below 230 K due to extreme line broadening and poor S/N ratio.) A similar behavior was observed in the powder spectrum (Fig. 2); on cooling the separation between the singularities and the shoulders remain essentially the same except that they are less well defined due to broadening.

Pake doublet-like spectra have been reported in a number of hydrated layered intercalates but is usually observed in association with a central component which has been assigned either to isotropically tumbling water molecules which lie outside the hydration shell and/or proton exchange.⁶⁻⁸ The absence of a central component in the ^1H NMR spectra shown in Figs. 2 and 4 clearly rules out the existence of either of these two processes in $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ and indicates similar motion for all interlamellar water molecules. It may also be concluded that there is no significant protonic contribution to the conductivity of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ which, then, must be due to mobile Na ions.

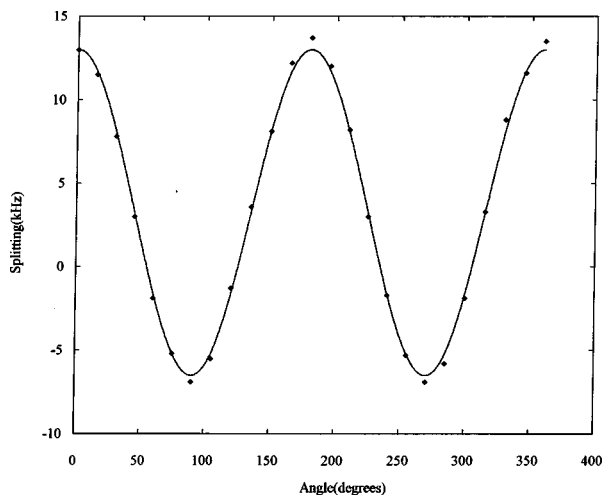


FIG. 3. Variation of the doublet splitting as a function of the angle, δ , between the normal to the layers of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ and the external magnetic field. The solid line is a plot of the function $\Delta = 13(3 \cos^2 \delta - 1)$.

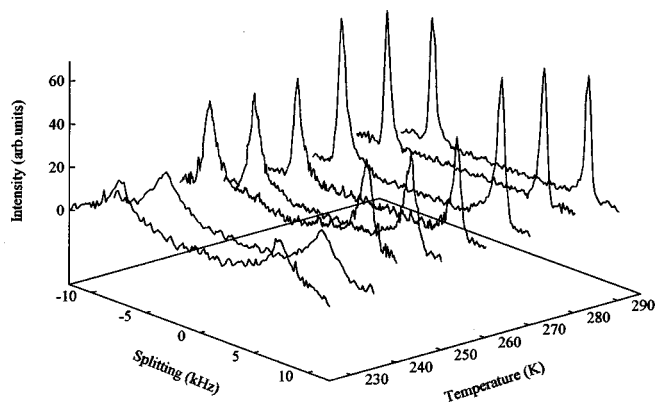


FIG. 4. ^1H NMR spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ crystal for $\delta = 0^\circ$ at different temperatures.

The ^1H NMR spectra (Figs. 2 and 4) correlates fairly well with the spectra expected of a solid in which nuclear spins occur in isolated pairs. In the case of isolated water molecules it is well known¹⁷ that intramolecular dipolar interactions give rise to a doublet with separation, $\Delta = \alpha(3 \cos^2 \theta - 1)/2$ where $\alpha = 3\gamma^2\hbar/r_{\text{H-H}}^3$ and θ is the angle between the interproton vector and the magnetic field and $r_{\text{H-H}}$ the interproton distance. For $r_{\text{H-H}}$ of 1.58 Å, corresponding to water molecules in their equilibrium geometry, $\alpha_{\text{equil}} = 91$ kHz. The fact that the ratio of the splitting for $\delta = 90^\circ$ and 0° in the crystal spectra is 1:2 and these values are close to that for the inner singularities and outer steps, respectively, of the powder spectrum (Fig. 2), implies that the intramolecular H-H vectors of all the interlamellar water molecules have the same orientation with respect to the \vec{C}^* axis. Assuming that $r_{\text{H-H}}$ of the intercalated water molecules is 1.58 Å, i.e., the water molecules maintain their equilibrium geometry even after intercalation, then the observed dipolar splitting would require an interpretation based on the motion of water molecules. A motion which satisfies the aforementioned requirements may be derived by considering the position of the interlamellar water molecules in $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ (Fig. 1). In this model the Na ion sits in an octahedral void formed by the two sets of three water oxygens. For a regular octahedra the sides of the equilateral triangle formed by the centers of the water molecules, would be the van der Waals diameter of a water molecule 2.8 Å. The \vec{C}_3 axis is parallel to \vec{C}^* , the normal to the layers. If the water molecules in the hydration shell rotate about the \vec{C}^* axis at a rate much greater than the frequency corresponding to the dipolar splitting ($\tau_{\text{rot}} \ll 10^{-5}$ s) then θ , the angle between the H-H vector and the magnetic field \vec{H}_o , fluctuates rapidly. The function $(3 \cos^2 \theta - 1)/2$ which is the second degree Legendre polynomial $P_2(\cos \theta)$ must be averaged for this free rotation, $P_2(\cos \theta) = P_2(\cos \delta) \cdot P_2(\cos \beta)$ where β , the angle between the \vec{C}^* axis and the H-H vector, is a constant and δ the angle between the \vec{C}^* axis and \vec{H}_o is the experimental variable (the definition of the angles is indicated in Fig. 5). The NMR spectra would therefore consist of two lines with splitting

$$\Delta = \alpha((3 \cos^2 \delta - 1)/2) \cdot ((3 \cos^2 \beta - 1)/2). \quad (1)$$

If $r_{\text{H-H}}=1.58 \text{ \AA}$ as in an isolated water molecule then α in Eq. (1) would have a value of $\alpha_{\text{equil}}=91 \text{ kHz}$. The experimentally observed angular dependence $\Delta=13(3 \cos^2 \delta - 1)/2$ then requires that β in Eq. (1) be 49.1 or 60.8° , depending on the sign of Δ . Correspondingly ψ the angle between the \vec{C}_2 axis of the water molecule and the \vec{C}^* axis, will have a value of 40.9 or 29.2° . ψ is also the angle between the \vec{C}_2 axis of the water molecule and the octahedral \vec{C}_3 axis thereby implying a trigonal elongation of the $\text{Na}(\text{H}_2\text{O})_6$ octahedra (for a regular octahedra $\psi=54.7^\circ$). This model is, however, in conflict with the observed crystallographic lattice expansion on intercalation, 5.6 \AA . A trigonally elongated octahedra would require a lattice expansion greater than twice the van der Waals diameter of the water molecule (2.8 \AA). If, on the other hand, the H-H vector of the water molecule, too, were to precess freely about the \vec{C}_2 axis then Eq. (1) would have to be modified to account for the further averaging due to this motion. This may be derived by considering the rapid rotation of the H-H vector around the \vec{C}_2 axis leading to the decomposition of $P_2(\cos \theta)$ as $P_2(\cos \phi) \cdot P_2(\cos \gamma)$ where ϕ is the angle between the \vec{C}_2 axis and \vec{H}_o and γ , the angle between the H-H vector and \vec{C}_2 axis of water molecule, is 90° . Rotation of the \vec{C}_2 axis of the water molecules in the hydration shell, about the \vec{C}^* axis would further decompose $P_2(\cos \phi)$ as $P_2(\cos \psi) \cdot P_2(\cos \delta)$. Thus if both rotations are present, $P_2(\cos \theta)=P_2(\cos \psi) \cdot P_2(\cos \delta) \cdot P_2(\cos \gamma)$ and the observed splitting

$$\Delta = \alpha_{\text{equil}}((3 \cos^2 \psi - 1)/2) \cdot ((3 \cos^2 \delta - 1)/2) \cdot ((3 \cos^2 \gamma - 1)/2). \quad (2)$$

The observed angular dependence of Δ can be satisfied for $\psi=67.8$ or 43.6° . The value of $\psi=67.8^\circ$ is similar to that obtained for hydrated ions in mica type silicate clays ($\psi=65^\circ$)⁷ and corresponds to $\text{Na}(\text{H}_2\text{O})_6$ octahedra being trigonally compressed. This may be achieved by an elongation of the sides of the equilateral triangle formed by the two sets of three water molecules. This network of octahedral hydration shells in which water molecules rotate around their \vec{C}_2 axis which is also the coordinate bond of the water oxygen to the Na ions and with the \vec{C}_2 axis in turn rotating around the \vec{C}^* axis would fit the geometrical requirements of the crystallographic interlayer lattice spacing as well as the NMR spectra. If the \vec{C}^* axis about which the \vec{C}_2 axis rotates, coincides with the \vec{C}_3 axis of the $\text{Na}(\text{H}_2\text{O})_6$ pseudo-octahedra (Fig. 5), the motion would correspond to rotation of the hydration shell as a whole. Such motion has been invoked for hydrated Na ions in the galleries of mica type silicates.⁷ If isolated $\text{Na}(\text{H}_2\text{O})_6$ polyhedra existed in the galleries a collective motion of the entire hydration shell may easily be envisaged. In $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ it is difficult to reconcile a rotational motion involving the hydration shell as a whole with the fact that the Na to H_2O stoichiometric ratio requires an edge sharing of the $\text{Na}(\text{H}_2\text{O})_6$ polyhedra. A water molecule would, therefore, be part of the hydration shell of more than one Na ion. In such situations one would expect the time averaged orientation of the water molecule towards these ions to be identical. A more likely motion, therefore, is one in which

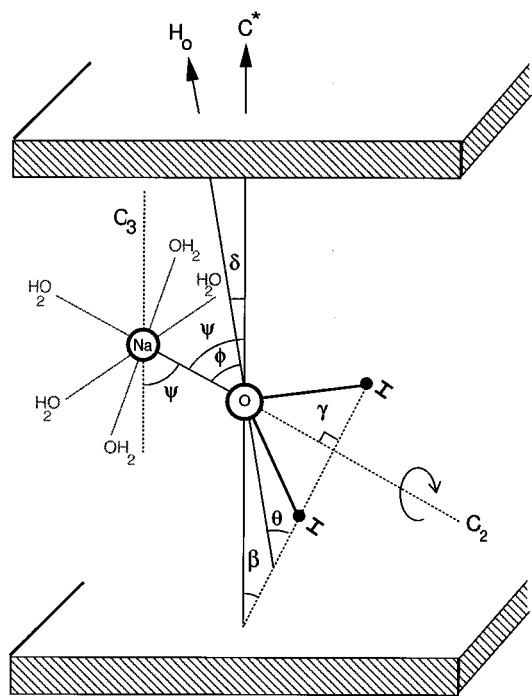


FIG. 5. Definition of the angles used in the analysis of the ^1H NMR spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$. The \vec{C}_3 axis of the $\text{Na}(\text{H}_2\text{O})_6$ octahedra and the \vec{C}_2 axis of the water molecule are shown as dotted lines.

the \vec{C}^* axis, about which rotation occurs, passes through the water molecule, i.e., a spinning motion of individual water molecules. This would allow the water molecule to maintain an identical orientation towards neighboring Na ions while at the same time satisfying requirements for the observed ^1H Pake doublet splitting and its angular dependence. It may be seen from Fig. 5 that rotation of the \vec{C}_2 axis of the water molecule about the \vec{C}^* axis as marked in the figure would allow the water molecule an identical time averaged orientation towards neighboring Na ions (Fig. 1). It may be emphasized that the choice between collective versus individual motion of the water molecules have to be arrived at from considerations other than the present NMR results. An explanation for the observed Pake doublet splitting and its angular dependence requires fast motion of the H-H vectors about the \vec{C}_2 axis and rotation of the \vec{C}_2 axis, in turn about the \vec{C}^* axis; it does not specify the nature of this motion.

The ^2H NMR of powder samples of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{D}_2\text{O})_2$ was also recorded. The spectrum showed a single quadrupolar powder pattern expected of an $I=1$ nuclei in an axial field (Fig. 6). The powders were not free flowing and showed considerable preferred orientation and consequently the spectrum is not a typical powder pattern. The separation of the inner singularities (38 kHz) and outer steps (76 kHz) are in the ratio 1:2, corresponding to a time averaged quadrupole coupling constant e^2qQ/h of 50.75 kHz . The position and separation of the doublet did not show any significant variation in the temperature range $290\text{--}360 \text{ K}$.

In many deuterated hydrates it has been observed that in the absence of rotation about the \vec{C}_2 axis of the water of crystallization, the two deuterium atoms are magnetically in-

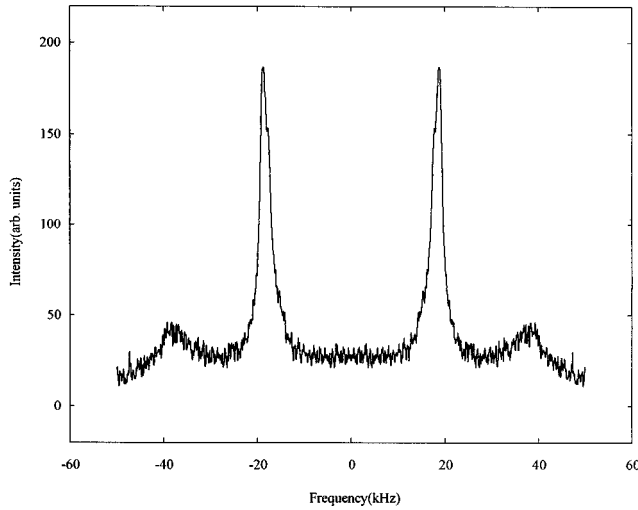


FIG. 6. ^2H NMR spectrum of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{D}_2\text{O})_2$ powder at 300 K.

equivalent and two sets of quadrupolar splittings are observed with the quadrupolar coupling constant e^2qQ/h typically equal to 225–250 kHz. When fast rotation about the C_2 axis is present, however, the e^2qQ/h values are scaled by half (120–130 kHz) and is the same for both deuterium atoms; only one averaged electric field gradient tensor is observed with the principal axis corresponding to the D–O–D bisector.¹⁸ Further reduction in the quadrupolar splitting would require additional motion to be invoked. Extending the above argument to the spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{D}_2\text{O})_2$ it may be seen that the ^2H NMR results are in agreement with the ^1H NMR results and its interpretation. The fast rotation about the \vec{C}_2 and \vec{C}^* axes required to explain the ^1H NMR spectra implies that all O–D bonds of the corresponding deuterated compound be equivalent and consequently the e^2qQ/h values for the ^2H nuclei identical. Derivation of geometrical parameters from the ^2H NMR spectra, as in the case of ^1H spectra, was however not attempted. This would have required an exact knowledge of the magnitude and orientation of the quadrupolar tensor for a ^2H nuclei of a D_2O molecule directly coordinated to a positively charged Na ion. In such situations, to assume that the value of e^2qQ/h is identical to that for a ^2H nuclei of a free or uncoordinated D_2O molecule would be in serious error.

In general ^2H NMR experiments are superior to ^1H NMR for studying the motion of molecules because of its higher angular resolution and negligible dipolar broadening. The present compound $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ is an exception in that, ^1H NMR, itself is able to provide detailed information. This is because the ^1H NMR spectrum resembles that of an isolated pair of spins. Moreover by recording the spectra on oriented crystals, sharp, well resolved lines (Fig. 4) which do not suffer from the effects of orientational distribution as observed in powder samples have been obtained, enabling quantitative interpretation of the ^1H spectra, in a straightforward manner.

The validity of Eq. (2) rests on the assumption that water molecules undergo rapid rotation around their \vec{C}_2 axis which, in turn, rotates rapidly about \vec{C}^* . The decomposition of the

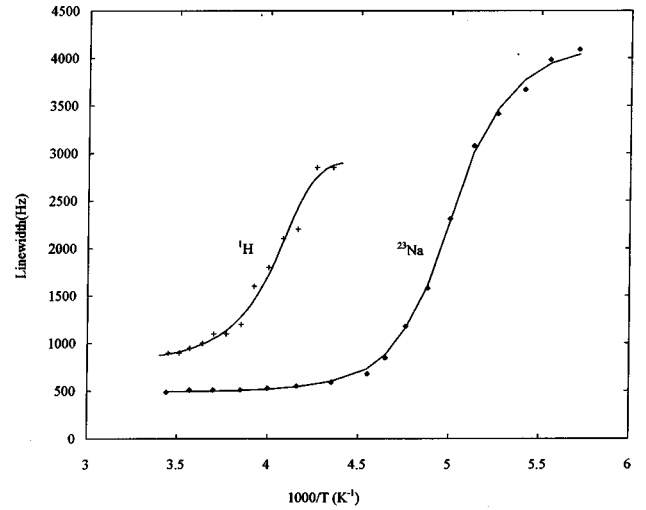


FIG. 7. ^{23}Na and ^1H NMR linewidths as a function of inverse temperature for $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$. Solid lines are a fit to Eq. (3).

Legendre polynomial $P_2(\cos \theta)$ in Eqs. (1) and (2) requires that the rotation be much faster than 91 kHz, the dipolar splitting observed for an isolated pair of protons separated by a distance of 1.58 Å. The intramolecular dipolar splitting, thus provides an internal probe for the motion of the water molecules as well as their orientation. The fact that the dipolar splitting does not change with temperature, implies from the above analysis, that the orientations of the water molecules do not change and the assumption of fast rotation about their \vec{C}_2 axis and the \vec{C}^* holds good in the range of temperatures investigated.

The temperature dependence of the linewidth of a component of the ^1H Pake doublet of a $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ crystal is shown in Fig. 7. The linewidth values and their temperature dependence show no angular variation. The linewidth may be related to a correlation time, τ_d , by the phenomenological relation¹⁷

$$\Delta\omega^2 = \Delta\omega_{\text{HT}}^2 + (2/\pi) \cdot \Delta\omega_{\text{RL}}^2 \arctan(\alpha\Delta\omega\tau_d), \quad (3)$$

where the numerical factor α is of order unity. $\Delta\omega_{\text{HT}}$ is the high temperature limiting linewidth and $\Delta\omega_{\text{RL}}$ the rigid lattice linewidth. Assuming an Arrhenius temperature dependence, $\tau_d = \tau_0 \exp(E_a/kT)$, Eq. (3) may be fitted to the experimental linewidth. The best fit was obtained for $E_a = 7.5$ kcal/mol and the pre-exponential factor, $\tau_0 = 3.5 \times 10^{-12}$ s (solid line in Fig. 7).

The temperature variation of the ^1H spin lattice relaxation time is shown in Fig. 8. A well defined minimum is observed in the T_1 versus temperature plot. The spin lattice relaxation rate, is related to the real part, $J'(\omega)$ of the complex spectral density function via¹⁷

$$1/T_1 = K[J'(\omega, T) + J'(2\omega, T)]. \quad (4)$$

The relaxation data of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ was analyzed using the Bloembergen–Purcell–Pound (BPP) model¹⁹ which requires that the correlation function $g(t)$, decay as a single exponential, $g(t) = \exp(-t/\tau_c)$. The resulting BPP expression for spin lattice relaxation times is given by

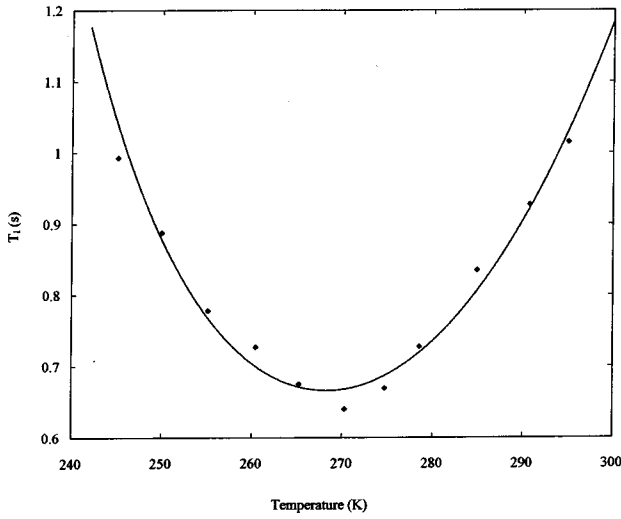


FIG. 8. Temperature variation of the ^1H NMR spin-lattice relaxation time of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$. The solid line is a fit to the BPP expression [Eq. (5)].

$$1/T_1 = K[\tau_c/(1 + \omega^2\tau_c^2) + 4\tau_c/(1 + 4\omega^2\tau_c^2)], \quad (5)$$

where K depends on the spin interaction responsible for the relaxation. Assuming τ_c has an Arrhenius temperature dependence, Eq. (5) may be fitted to the experimental data. The fit shown as a solid line in Fig. 8 was obtained for $E_a = 6.3$ kcal/mol and $K = 3.2 \times 10^8 \text{ s}^{-2}$. The correlation time τ_c varies from 7.3×10^{-10} s at 300 K to 1.5×10^{-8} s at 230 K.

The proton spin-lattice relaxation would have contributions from both intra- as well as intermolecular interactions, $1/T_1 = 1/T_{1\text{ inter}} + 1/T_{1\text{ intra}}$. $T_{1\text{ inter}}$ has contribution from both intermolecular homo- and heteronuclear interactions. These would be modulated by the motion of the water molecules in the hydration shell. $T_{1\text{ intra}}$, due to intramolecular proton-proton interactions, however would reflect the correlation times associated with the rotations of the water molecules about their \vec{C}_2 axis. The fact that the proton T_1 data fits well to the BPP expression suggests that the temperature dependence in this temperature range is due to a single mechanism. For a purely intramolecular interaction the value of K in Eq. (5) may be calculated assuming the interproton distance as in a free water molecule. For intramolecular homonuclear interactions, $K = 2\gamma^4\hbar^2 I(I+1)/5r_{\text{H-H}}^6$, which for $r_{\text{H-H}} = 1.58 \text{ \AA}$ is $2.8 \times 10^8 \text{ s}^{-2}$. This value is close to that obtained from the BPP fit suggesting that the temperature dependence of the T_1 data in the temperature range shown in Fig. 8 is due to intramolecular interactions and the correlation time, τ_c , likely to be characteristic of the rotational motion of the interlamellar water molecules about their \vec{C}_2 axis. The value of the activation barrier 6.3 kcal/mol obtained from the fit is also close to that reported for rotation about the \vec{C}_2 axis for water molecules in hydrates (≈ 6.2 kcal/mol).¹⁸ These results imply that the time scale associated with rotation of the water molecules about the \vec{C}_2^* axis is very different—much faster or much slower—than τ_c obtained from the data of Fig. 8. The minimum in the T_1 versus temperature data corresponding to this motion would, therefore, occur at temperatures much higher or much lower than that of Fig. 8. Measurements at

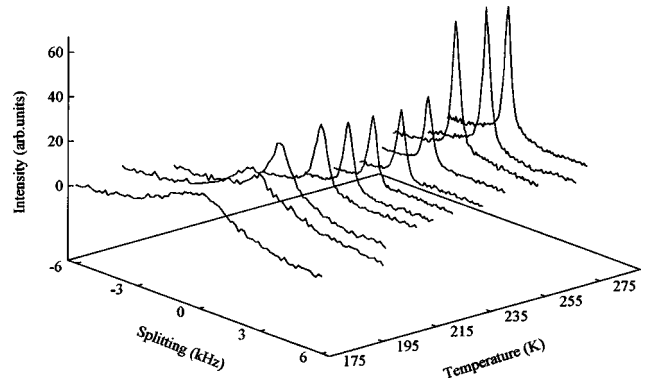


FIG. 9. ^{23}Na NMR spectra of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ at different temperatures.

these temperatures, however, was not possible; at low temperatures there is considerable line broadening and hence poor data quality for an inversion-recovery T_1 experiment while at higher temperatures there is loss of water and decomposition of the sample.

B. ^{23}Na NMR spectroscopy

The static ^{23}Na NMR spectrum of a powder sample of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ shows a single Lorentzian line at room temperature with a FWHM of 480 Hz. On cooling the line broadens to a FWHM value of 4.1 kHz at 175 K (Fig. 9). The ^{23}Na NMR spectra were recorded with a spectral width of 250 kHz but the $\pm 3/2 \leftrightarrow \pm 1/2$ satellites could not be observed. The room temperature ^{23}Na NMR in the bilayer hydrated mica type silicate clays, in which NA environments are similar to that in the present sample, also show only a single line (FWHM)=1 kHz.²⁰ In the NMR spectra of the clays, too, no satellites were observed and the reduction of linewidths on magic angle spinning was less than half the static linewidth. The linewidth of the NMR spectra of Fig. 9 is a measure of the dipolar coupling of the ^{23}Na with neighboring spins and, possibly, second order quadrupolar coupling and chemical shift anisotropy. These interactions are averaged by the increased mobility of the Na ions at higher temperatures, leading to a decrease in the linewidth.

The temperature variation of the ^{23}Na linewidth (Fig. 7) shows a similar trend as the ^1H linewidths and may be fitted using Eq. (3). The best fit (solid line in Fig. 7) was obtained for an Arrhenius activation energy $E_a = 7.3$ kcal/mol and a pre-exponential factor $\tau_o = 4.7 \times 10^{-12}$ s; these values are close to those obtained from the fitting of the ^1H linewidth data. The temperature variation of ^{23}Na spin lattice relaxation times (Fig. 10), however, is quite different from that of the proton (Fig. 8). The ^{23}Na T_1 shows a broad poorly defined minima and obviously cannot be fitted using the BPP expression for a single exponential decay function. Neither is the temperature dependence of the ^{23}Na T_1 characteristic of the spin-lattice relaxation expected for a distribution of correlation times, e.g., the Cole-Cole, Cole-Davidson, or Haveriliak-Negami distribution functions.²¹ The data of Fig. 10 suggests that the correlation function may be temperature dependent so that attempts to interpret the data assuming a temperature independent decay function with Arrhenius ac-

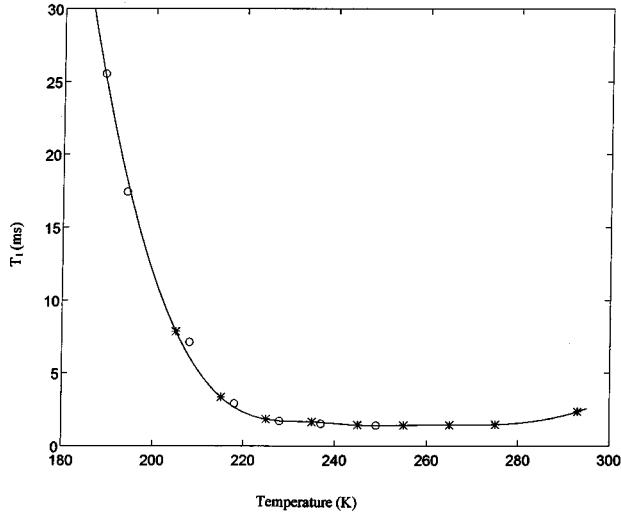


FIG. 10. Temperature variation of the ^{23}Na NMR spin-lattice relaxation time (*). The circles (O) are the values calculated from the frequency dependent conductivity. The solid line is a guide to the eye.

tivated decay times would be unsuccessful. The temperature variation of ^{23}Na T_1 is discussed in a subsequent section.

C. Impedance spectroscopy

In order to understand the origin of the ^{23}Na T_1 behavior frequency dependent impedance measurements were carried out. The close relation between the spin lattice relaxation (SLR) and electrical conductivity relaxation (ECR) has been pointed out by various workers,^{9–11} the two can usually be described by similar decay functions. Two alternative formalisms are usually employed in the analysis of ECR, the conductivity formalism in the frequency domain and the electrical modulus formalism from which a conductivity decay function in time domain may be derived. In the latter formalism the electric modulus M^* ($=1/\epsilon^*$) is expressed as

$$M^*(\omega) = M_\infty \left[1 - \int_0^\infty (-d\Phi/dt) e^{-i\omega t} dt \right], \quad (6)$$

where $\Phi(t)$, the electrical conductivity relaxation, is the decay of the electrical field at constant displacement vector due to the conduction process.^{22,23} A previous analysis of the impedance data of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ in the modulus formalism⁵ found that the ECR followed a Kohlrausch–William–Watts (KWW) or stretched-exponential decay function:

$$\Phi(t) = \exp(-t/\tau_{\text{SE}})^\beta \quad 0 < \beta < 1.$$

It was found that in $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ the value of the β parameter which represents an index of correlation among charge carriers, increases with increasing temperature.⁵ The departure of β from unity is a measure of the deviation from a single exponential Debye-like relaxation.

In the conductivity representation the dispersion of the real part of the conductivity $\sigma'(\omega) = i\omega\epsilon^*(\omega)$, where ϵ^* is the imaginary component of the complex permittivity is analyzed. The dispersion of $\sigma'(\omega)$ of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ at

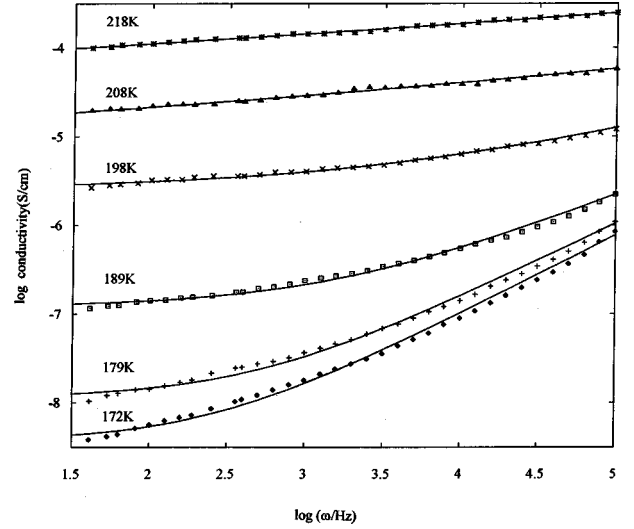


FIG. 11. Conductivity versus frequency for $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$, presented in a double logarithmic scale, at different temperatures. Solid lines are fits to the expression in Eq. (7).

various temperatures is shown in Fig. 11. $\sigma'(\omega)$ shows a sublinear frequency dispersion and follows a simple power law.^{24,25}

$$\sigma'(\omega) = \sigma_{\text{dc}} + A\omega^s, \quad (7)$$

where σ_{dc} is the dc conductivity, A a temperature dependent parameter, and s a fractional exponent between 0 and 1. This behavior is characteristic of hopping conductivity and has been “universally” observed in a number of ionic conductors. The fractional exponent, s , has been interpreted to appear as a result of correlation among charge carriers. For a single exponential Debye-like ECR the exponent s in Eq. (7) is zero. In $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ the value of the conductivity exponent decreases with increasing temperature (Fig. 12). In the light of the NMR results the charge carriers in $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ may be identified as the Na ions. The impedance measurements indicate a non-Debye-like behavior of the ECR in $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ due to slowing down

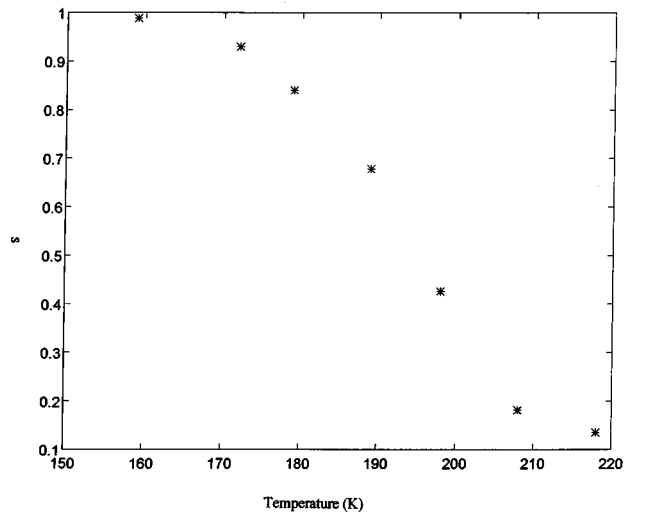


FIG. 12. Temperature variation of the fractional exponent s used in Eq. (7).

of the relaxation process as a result of Coulombic correlation among Na ions. The extent of correlation is temperature dependent, being much stronger at lower temperatures. The ECR is almost Debye like at higher temperatures.

D. Electrical conductivity relaxation and ^{23}Na spin lattice relaxation: A comparison

The impedance measurements and ^{23}Na NMR are in qualitative agreement. The impedance measurements indicate that ECR decay functions are temperature dependent since the extent of correlation among the charge carriers varies with temperature. Similarly the temperature variation of the ^{23}Na spin lattice relaxation (SLR) suggests a temperature dependent correlation function. A more quantitative comparison may be made if we *assume* that $\sigma^*(\omega)$ may be reasonably well approximated as a single particle conductivity related to the ions self-diffusion coefficient via the Nernst–Einstein relation. In such situations the SLR and ECR may both be expressed in terms of the frequency spectrum obtained from the Fourier transform of the same auto-correlation decay function $\Phi(t)$.⁹ The desired relation between the SLR and ECR may be obtained by eliminating $\Phi(t)$ from the expressions of T_1 and $\sigma^*(\omega)$. We derive this relation for a situation where the conductivity exhibits a power law dispersion. The electric modulus M^* is related to the Fourier transform of the time derivative of the ECR correlation function, $\dot{\Phi}(t)$, henceforth written as $\hat{\Phi}(\omega)$. Equation (6) may be rewritten as

$$M^*(\omega) = (1 + \hat{\Phi}(\omega)) / \epsilon_\infty. \quad (8)$$

Since $\hat{\Phi}(\omega) = i\omega\hat{\Phi}(\omega) - 1$, the modulus may also be expressed in terms of the Fourier transform of the correlation function

$$M^*(\omega) = i\omega\hat{\Phi}(\omega) / \epsilon_\infty. \quad (9)$$

The electric modulus, $M^* = 1/\epsilon^*$, may be written in terms of the conductivity since $\epsilon^*(\omega) = [(\sigma^*(\omega)/i\omega) + \epsilon_\infty]$. Substituting in Eq. (9) one obtains

$$\hat{\Phi}(\omega) = 1 / [(\sigma^*(\omega) / \epsilon_\infty) + i\omega]. \quad (10)$$

For an ideal Debye case $\sigma^*(\omega) = \sigma_{\text{dc}}$ and the ECR rate is simple $\sigma_{\text{dc}}/\epsilon_\infty$ but for frequency dependent conductivity it has a spectrum of the form $\sigma^*(\omega)/\epsilon_\infty$.

If $\sigma^*(\omega)$ is essentially a single particle conductivity, the spectral density function $J^*(\omega)$ may be obtained via the Nernst–Einstein relation:⁹

$$J^*(\omega) = 1 / [(\sigma^*(\omega) / \epsilon_\infty)(T/T_o) + i\omega], \quad (11)$$

where $T_o = (nq^2x_o^2)/6\epsilon_o k_B$, n is the concentration of mobile ions, q and x_o are the charge and hopping distances and k_B the Boltzmann constant. T_o depends on the material properties of the compound. Since the conductivity of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ obeys a power law the above expression may be further simplified. The real, σ' , and imaginary, σ'' , components of the conductivity are related by the Kramers–Krönig transform.²⁶ For power law

behavior $(\sigma'(\omega) - \sigma_{\text{dc}}) / \sigma''(\omega) = \cot(s\pi/2)$ or $\sigma''(\omega) = A\omega^s \tan(s\pi/2)$. Substituting for $\sigma'(\omega)$ and $\sigma''(\omega)$ in Eq. (11),

$$J^*(\omega) = 1 / [(\sigma_{\text{dc}} + A\omega^s)(T/T_o\epsilon_\infty) + i(\omega + A\omega^s \tan(s\pi/2))(T/T_o\epsilon_\infty)]. \quad (12)$$

The T_1 rates at any temperature may therefore be calculated from Eq. (4) using the values of σ_{dc} , A and the exponent s obtained from fitting the frequency dependent conductivity to power law [Eq. (7)]. The T_1 values as obtained from the conductivity data of Fig. 11 are shown in Fig. 10. The calculated T_1 values are for $K = 4.2 \times 10^{10} \text{ s}^{-2}$ and $T_o = 503 \text{ K}$ obtained by floating these parameters in the fitting procedure. Since there are no paramagnetic impurities present in $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ the observed value of K could be due to either dipolar or quadrupolar relaxation mechanisms. These values are similar to those reported on other ionically conducting solids.^{9,10}

The agreement between the T_1 values calculated from the conductivity and those obtained from the NMR experiment are surprisingly good. In many ionic materials, e.g., ionic glasses, the observed relaxation as probed by nuclear spin relaxation is quite different from that probed by conductivity measurements. As shown by Ngai²⁷ these differences arise from the fact that the $\sigma^*(\omega)$ is not strictly a single-particle conductivity and therefore additional cross-correlation terms between ions appear in the conductivity correlation function which are absent in the SLR correlation function. Moreover if the mechanism of the SLR is dipolar in origin, the contribution of ion pairs at shorter distances to the SLR correlation function would be more significant since the dipolar interaction varies as $1/r_{ij}^3$. It has, however, been pointed out by Ngai²⁷ that these factors would be more significant at higher ion concentrations. In $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ the good agreement between the T_1 values is probably because the number density of Na ions in the interlamellar space is small so that the mean distance between the Na ions is 8.1 Å. (The distance of closest approach is 4.8 Å). It had been shown previously that the ECR follows a stretched exponential decay function with a temperature dependent exponent.⁵ It follows from Fig. 10 that the SLR, too, may be described by a similar function.

E. Motion of the hydrated Na ion

In $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ interlamellar Na ions are mobile and responsible for the conductivity. At the same time, as had been shown in the preceding section, the proton spectra exhibits a Pake doublet and no other features indicating that *all* interlamellar water molecules have similar orientation and undergo identical motions. The ^1H dipolar splitting and the ^2H quadrupolar splitting show no variation with temperature implying that water molecules in the ion's hydration shell maintain the same orientation and rotational motion at all temperatures. Since the Na ions are mobile this can be realized, only if the hydration shell moves along with the Na ions or in other words the relaxation of the hydration shell during the ions motion is much faster than the intramolecular ^1H dipolar interactions of the H_2O molecule (91 kHz). The

observed dipolar splitting and its angular variation requires that the diffusive motion of the hydrated ions be such that \vec{C}_3 of the pseudo-octahedral hydration shell remains parallel to the \vec{C}^* axis (the normal to the layers) so that the orientation of the \vec{C}_2 axis of the water molecule with respect to the \vec{C}^* axis is retained at all temperatures. The motion of the hydrated ion in the galleries is such that no further averaging of the intramolecular ^1H dipolar interactions occurs with increasing temperature. Ordering of water molecules due to the negatively charged $\text{Cd}_{0.75}\text{PS}_3$ layers is unlikely. If it were so, an orientation with the H_2O protons close to the layer would have been preferred as observed for intercalated water molecules in hydrotalcites.²⁸ Moreover, in a closely related compound $\text{Cd}_{0.75}\text{PS}_3\text{K}_{0.5}(\text{H}_2\text{O})$, where in fact the gallery height is less, isotropically rotating water molecules have been observed by both NMR²⁹ and dielectric measurements.³⁰

Further corroboration that Na ions in the galleries of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ move along with their hydration shell is the fact that the Arrhenius activation energies describing the temperature dependence of the ^1H and ^{23}Na NMR linewidths are almost identical, 7.3 and 7.5 kcal/mol, respectively, and the pre-exponential factors of the same magnitude ($\approx 10^{-12}$ s). This could arise only if the motional narrowing of the ^1H and ^{23}Na NMR linewidths arise from the same dynamics process namely anisotropic motion of the hydrated ion as a whole within the galleries. These results suggest that the conductivity of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ is not due to hopping of Na ions between octahedral vacancies of a rigid interlamellar H_2O bilayer but by the anisotropic sliding motion of the Na ion along with its hydration shell within the galleries. Stoichiometry considerations also rule out a hopping contribution to the long-range conductivity of $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$, since the density of interlamellar water indicates that the H_2O bilayer (Fig. 1) is not infinite but broken up into finite sized clusters. Hopping of Na^+ ions within such a cluster would at best manifest as a dielectric response, but the fact that the conductivity dispersion is well described by the power law of Eq. (7), suggests that such a response, too, is absent. The NMR results are in agreement with the above observations.

The power law behavior of the frequency-dependent conductivity is characteristic of non-Debye-like behavior arising from Coulomb correlation among charge carriers. The spin-lattice relaxation T_1 values calculated from the conductivity data are in good agreement with the measured ^{23}Na T_1 relaxation rates. It may, therefore, be concluded that the motion of the interlamellar hydrated Na ions are correlated through their mutual Coulomb interactions. The proton T_1 , however, indicates that in the temperature range studied, the rotational motion of the H_2O molecules in the hydration shell may still be described by a single exponential Debye-like relaxation.

In conclusion the present studies have shown that the conductivity of the layered $\text{Cd}_{0.75}\text{PS}_3\text{Na}_{0.5}(\text{H}_2\text{O})_2$ arises from the anisotropic motion of the hydrated Na ion in the galleries. The motion of the hydrated ion is such that the orientation of the \vec{C}_2 axis of the H_2O molecules with respect to the normal to the layers, \vec{C}^* , is always preserved.

- ¹R. Clement, I. Lagadic, A. Leautic, J. P. Andiere, and L. Lomas, *Chemical Physics of Intercalation II* NATO ASI Ser., Ser. B 315 (1993).
- ²G. Ouvrard, R. Brec, and J. Rouxel, *Mater. Res. Bull.* **20**, 1181 (1985).
- ³P. Jeevanandam and S. Vasudevan, *Solid State Ionics* **104**, 45 (1997).
- ⁴G. Sposito and R. Prost, *Chem. Rev.* **82**, 553 (1982).
- ⁵P. Jeevanandam and S. Vasudevan, *J. Phys. Chem. B* **102**, 3082 (1998).
- ⁶W. Müller-Warmuth, in *Physics and Chemistry of Materials with Low-dimensional Structures*, Vol. 17, edited by W. Müller-Warmuth and R. Schöllhorn (Kluwer Academic, Dordrecht, Netherlands, 1994), p. 339.
- ⁷J. Hougardy, W. E. E. Stone, and J. J. Fripiat, *J. Chem. Phys.* **64**, 3840 (1976).
- ⁸U. Röder, W. Müller-Warmuth, and R. Schöllhorn, *J. Chem. Phys.* **70**, 2864 (1979); U. Röder, W. Müller-Warmuth, and R. Schöllhorn, *J. Chem. Phys.* **75**, 412 (1981); U. Röder, W. Müller-Warmuth, H. W. Spiess, and R. Schöllhorn, *J. Chem. Phys.* **77**, 4627 (1982).
- ⁹K. Funke and D. Wilmer, *Europhys. Lett.* **12**, 363 (1990).
- ¹⁰C. Leon, J. Santamaria, M. A. Paris, J. Sanz, J. Ibarra, and L. M. Torres, *Phys. Rev. B* **56**, 5302 (1997).
- ¹¹C. Leon, M. L. Lucia, J. Santamaria, M. A. Paris, J. Sanz, and A. Varez, *Phys. Rev. B* **54**, 184 (1996).
- ¹²K. L. Nagai, in *Effects of Disorder on Relaxational Processes*, edited by R. Richert and A. Blumen (Springer-Verlag, Berlin, 1994), p. 88.
- ¹³W. Klingen, R. Ott, and H. Hahn, *Z. Anorg. Allg. Chem.* **396**, 271 (1973).
- ¹⁴D. O'Hare, J. S. O. Evans, P. A. Turner, S. Mason, S. J. Heyes, and J. Greenwood, *J. Mater. Chem.* **5**, 1383 (1995).
- ¹⁵B. A. Boukamp, *Solid State Ionics* **11**, 339 (1984); P. Jeevanandam, Ph.D. Thesis, Indian Institute of Science, Bangalore (1997).
- ¹⁶P. B. Macedo, C. T. Moynihan, and R. Boese, *Phys. Chem. Glasses* **13**, 171 (1972).
- ¹⁷A. Abragam, in *Principles of Nuclear Magnetism* (Oxford University Press, Oxford, 1961).
- ¹⁸L. W. Reeves, in *Progress in NMR Spectroscopy*, edited by J. W. Emsley, J. Feeney, and L. H. Sutcliffe (Pergamon, New York, 1969), Vol. 4, p. 230.
- ¹⁹N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).
- ²⁰V. Laperche, J. F. Lambert, R. Prost, and J. J. Fripiat, *J. Phys. Chem.* **94**, 8821 (1990).
- ²¹P. A. Beckmann, *Phys. Rep.* **171**, 85 (1988).
- ²²C. T. Moynihan, L. P. Boesch, and N. L. Laberge, *Phys. Chem. Glasses* **14**, 122 (1973).
- ²³C. A. Angell, *Chem. Rev.* **90**, 523 (1990).
- ²⁴S. R. Elliot, *Adv. Phys.* **36**, 135 (1987).
- ²⁵S. R. Elliot, *Solid State Ionics* **27**, 131 (1988).
- ²⁶A. K. Jonscher, *Dielectric Relaxation* (Chelsea Dielectrics, London, 1983).
- ²⁷K. L. Nagai, *J. Chem. Phys.* **98**, 6424 (1993).
- ²⁸A. van der Pol, B. L. Mojet, E. van de Ven, and E. de Boer, *J. Phys. Chem.* **98**, 4050 (1994).
- ²⁹N. Arun, M. S. Thesis, Indian Institute of Science, Bangalore, India (1996).
- ³⁰P. Jeevanandam and S. Vasudevan, *J. Chem. Phys.* **108**, 1206 (1998).