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DEUTERIUM NMR OF PYRIDINE INTERCALATED CADMIUM CHALCOGENOPHOSPHATE

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Abstract—Deuterium NMR spectra of the intercalation complexes of lamellar $Cd_2P_2S_6$ with various deuterated pyridine molecules are reported. The measurements indicate that the pyridine molecules lie within the chalcogen van der Waals gaps with their molecular planes parallel to the chalcogen layers. Between room temperature and −60°C the pyridine molecules reorient rapidly (on the NMR time scale) about an axis perpendicular to their molecular plane.

Keywords: Deuterium NMR, layered compound, intercalation compound, transition-metal chalcogenophosphates, pyridine intercalated lamellar semiconductor.

INTRODUCTION

Transition-metal chalcogenophosphates form a series of lamellar broad-band semiconductors with the general chemical formula $M_2P_2X_6$ (M = Mn, Fe, Cd, Ni, Mg and X = S, Se). The basic structural unit of these compounds is a sandwich of three covalently bonded atomic layers in which the middle one contains the metal atoms and P_2 pairs (in a ratio 2:1) while the chalcogen atoms occupy the outer layers (see Fig. 1). In the crystals these units are stacked on top of each other and held together via weak van der Waals (VDW) bonds. At ambient temperatures the transition metal sulfides are reported to be either monoclinic or rhombohedral and the selenides to be rhombohedral [1–5].

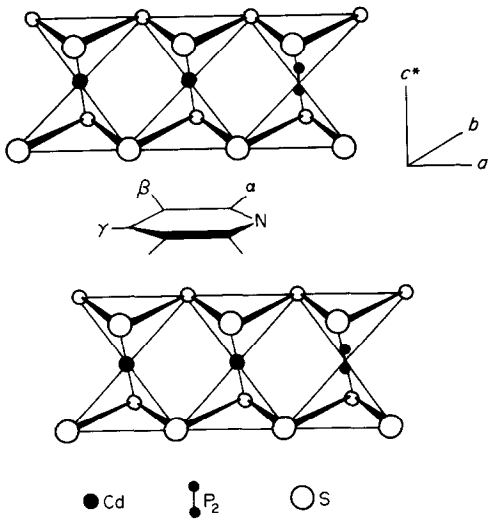

Fig. 1. The layered structure of $Cd_2P_2S_6$ viewed parallel to the chalcogen layer with a pyridine molecule in the VDW gap.

Under appropriate conditions, guest molecules or atoms can intercalate the VDW regions resulting in dramatic changes in the physical properties of the materials [6–10]. The most common intercalates are alkali metals, organometallic complexes and amines, suggesting that the driving force for intercalation may involve redox reactions. Several techniques have been used to study structural and dynamic characteristics of these intercalation compounds, including X-ray diffraction [6, 7], dielectric relaxation [11], electrical conductivity [9], IR [12], ESR [11] and NMR (particularly ^1H) [13–19]. The various techniques have their specific advantages and limitations. To this list we now add deuterium NMR which proved to be a powerful tool in the study of ordered systems [20–23] such as molecular crystals, inclusion compounds, polymers and liquid crystals, but has apparently not been used so far for chalcogenophosphate complexes of the type described above. The system chosen for our study consists of monoclinic $Cd_2P_2S_6$ (space group $C2/m$) intercalated with several isotopic species of deuterated pyridine. The results show that the pyridine molecules are oriented parallel to the chalcogen layers and undergo fast rotational motion about an axis perpendicular to the molecular plane.

These conclusions are derived from the magnitude and orientation dependence of the quadrupole interaction of the pyridine deuterons: a specific deuteron

in an ordered sample exhibits a two-line spectrum with splitting $\nu = 3/2\ (e^2qQ/h)\langle 1/2\ (3\cos^2\theta - 1)\rangle$, where e^2qQ/h is the principal component of the quadrupole interaction (assumed to be axially symmetric, $\eta = 0$, about the C–D bond direction), θ is the instantaneous angle between the C–D bond and the magnetic field, and the angular brackets indicate averaging over fast motions (on the NMR time scale). Thus using differently oriented samples, dynamic and structural information about intercalated molecules can be obtained from their deuterium NMR.

EXPERIMENTAL

Material

Single crystals of $Cd_2P_2S_6$ were prepared by sealing stoichiometric amounts of CdS, sulfur and red phosphorus in an evacuated Vycor tube and heating in a two-zone (600°C bottom and 720°C top) furnace [3, 24] for about 6 days. The resulting product consisted of crystalline platelets ($5 \times 5 \times 0.1\ mm^3$) whose planes were parallel to the crystallographic *ab* layers. Chemical analysis gave Cd: 44.9, S: 42.18 and P: 12.82 in agreement with the chemical formula. Intercalation was affected by heating single crystals of $Cd_2P_2S_6$ sealed with pyridine in Pyrex tubes to ~80°C for 3 days. This process turned the crystals deep yellow and gravimetric analysis indicated that the stoichiometry of the complex was $Cd_2P_2S_6$ (pyridine)$_1$.

Three types of deuterated pyridine species were used, namely perdeuterated pyridine (pyridine-d_5, obtained from Merck, Darmstadt), monodeuterated pyridine-d_α and monodeuterated pyridine-d_β. The latter two compounds were synthesized in our laboratory from the corresponding monobromopyridines by dehalogenation with Zn/D_2SO_4 in D_2O under reflux [25]. The product was precipitated as a pyridine–$HgCl_2$ complex which was carefully dried and subsequently decomposed by heating with NaOH in a vacuum manifold. The pyridine was collected in a liquid nitrogen cold trap, intensively dried over solid KOH and purified by repeated distillation. The products were checked by mass spectroscopy, liquid chromatography and ^1H NMR, and found to be of better than 98% purity. The level of isotopic labelling was higher than 95%.

NMR measurements

The deuterium NMR (46.07 MHz) spectra were obtained on a Bruker CXP-300 spectrometer using a horizontal solenoid (5 mm i.d.), high power probe equipped with a variable temperature unit. The samples were made up by stacking together 10–20 crystallites between a thin glass slide with their crystallographic c^*-axes parallel to each other, but with random orientation of the *a*- and *b*-axes (c^* is perpendicular to the *ab* plane). Orientation dependent spectra were obtained by rotating the sample relative to the magnetic field within the solenoid coil. The rotations were made about an axis perpendicular to the stacking direction in such a way that the c^*-axis spanned all orientations parallel and perpendicular to the field direction. The sample orientation could be determined to within ~5°. Spectra were recorded using the phase alternate quadrupole echo method with 4.5 μs $\pi/2$ pulses and 30 μs between pulses. Recycling time was adjusted to avoid saturation and was usually set at 1 s.

RESULTS AND DISCUSSION

The temperature and orientation dependence of the deuterium NMR of samples made up from different isotopic pyridine species were studied. Examples of spectra with the crystallographic c^*-axis oriented both parallel and perpendicular to the magnetic field (H_0) are shown in Fig. 2. The sharpness of the peaks for both orientations indicates that the samples are well oriented and that whatever motion is present it is fast on the NMR time scale. Moreover the splittings in the spectra for $H_0 \perp c^*$ are within the experimental accuracy of those for the corresponding $H_0 \| c^*$ spectra. An additional rotation experiment shows that the splittings obey a $(3\cos^2\alpha - 1)$ dependence, indicating that the average quadrupole tensors are uniaxial (or very nearly so). Comparison of the spectra from the d_α, d_β and perdeuterated pyridine species allows unambiguous assignment of the various peaks. From the spectra with $H_0 \| c^*$ the following splittings are obtained: $\nu^\alpha = 127$ kHz; $\nu^\beta = 168$ kHz; $\nu^{\bar{}} = 122$ kHz. These splittings are about half those expected for aromatic deuterons suggesting that all C–D bonds lie in a plane perpendicular to the c^*-axis. The most likely interpretation

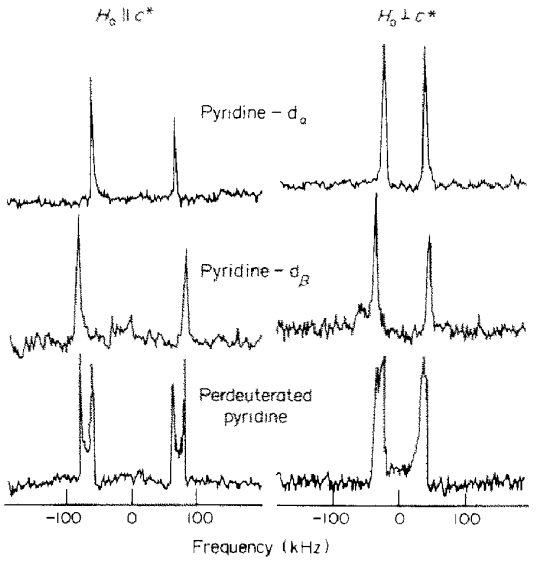

Fig. 2. The deuterium NMR spectra of $Cd_2P_2S_6$ intercalated with pyridine-dα, pyridine-d_β and perdeuterated pyridine at two different orientations with respect to the magnetic field as indicated in the figure.

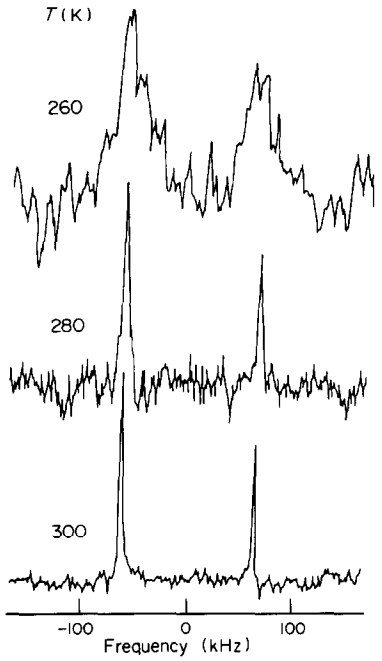

Fig. 3. Deuterium NMR spectra of pyridine-d_α in $Cd_2P_2S_6$ as a function of temperature with $H_0 \| c^*$.

of this result is to assume that the pyridine molecules lie in the VDW gap with their planes parallel to the lamellar *ab* planes. Since the spectra remain sharp in all orientations we must conclude that the pyridine molecules reorient rapidly within the VDW gap about an axis normal to the molecular plane. This conclusion is consistent with previous results in $MnPSe_3(pyridine)_{0.25}$ studied by one-dimensional electron density projection [9]. However, it is different from the pyridine molecular orientation in analogous layered compounds such as NbS_2 and TaS_2 [26–28] in which the pyridine planes orient normal to the MS_2 slabs with the nitrogen atoms midway between the slabs. None of these studies reported dynamical processes of the pyridine guest molecules.

Comparison of the splittings from the various deuterons shows an exceptionally high value for d_β. It is difficult to explain this result on geometrical grounds without abnormally twisting the β-hydrogens out of the pyridine plane. A more likely interpretation is to assume that the β-deuterons are associated with much larger quadrupole interactions than normally found for aromatic deuterons. We have not found evidence for this abnormality in previous theoretical [29] or experimental [30, 31] studies of pyridine. In fact the quadrupole interactions of the various deuterons in liquid crystalline solutions [28] differed by less than about 10% as compared to 30% found in the present case. It is possible that the effect is unique to the intercalation complexes and reflects a specific interaction between the chalcogenophosphate layers and the pyridine molecules which results in an abnormally high e^2qQ/h or asymmetry parameter for the deuterons.

We have also carried out variable temperature experiments in order to check whether the molecular reorientation process can be frozen out. Examples of spectra for pyridine-d and $H_0 \| c^*$ are shown in Fig. 3. No significant change in either the splitting or the linewidth occurs down to about $-60°C$, however, on further cooling the spectrum broadens and eventually escapes detection. The origin of this broadening is not that clear since freezing-out of the planar reorientation should not affect the linewidth at this orientation. It is possible that the line broadening reflects a dispersion in the orientation of the layers on cooling.

The present investigation has shown that pyridine guest molecules are oriented with their planes parallel to the host lattice internal surface of $Cd_2P_2S_6$. This arrangement minimizes direct interaction of the nitrogen lone pair with the host lattice. At the temperature range studied, the pyridine molecules undergo fast planar rotational motion about an axis perpendicular to the molecular plane in the van der Waals gap.

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