

Magnetic Resonance Studies of Intercalation Compounds: A Selective Review

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ABSTRACT

This review highlights some of the recent progress in understanding intercalation compounds through magnetic resonance techniques and some of the recent advances in magnetic resonance techniques for studying the chemistry and physics of such systems.

INTRODUCTION

During the last three or four years, nearly two hundred papers have been published that used NMR or ESR spectroscopy to study compounds formed by the intercalation of molecules or ions into the van der Waals gap of a layered host compound. The host lattices have ranged from the simple, such as graphite, to the complex, such as clay. In many cases, magnetic resonance techniques now enable one to obtain quite detailed information on even fairly complex intercalated species, on the nature of the changes in the host lattice accompanying intercalation, and on the nature of the interactions between the intercalant species and the host lattice. Magnetic resonance is used in conjunction with many other techniques to obtain a fuller picture of these interesting systems, but this review will limit its focus to the use of NMR and ESR techniques.

DISCUSSION

The past few years have seen a substantial increase in the number of studies of ternary systems, systems in which two chemical species are introduced into the van der Waals gap. We begin by noting multiple advances in understanding some of the ternary systems in which both a metal, such as potassium, and ammonia, NH_3 , are co-intercalated into either graphite or a metal sulfide. Using highly-oriented pyrolytic graphite (HOPG), Resing and coworkers in a

series of papers [1,2] have observed both the proton-proton dipolar splitting and the ^{14}N -proton dipolar splitting in the ^1H spectrum as a function of the orientation of the graphite intercalation compound (GIC) in the magnetic field, H_0 . Based on earlier work on similar systems [3], these spectra indicate that these dipolar splittings are motionally averaged by rapid reorientation of ammonia about its C_3 -axis, which is oriented parallel to the graphene planes, and by rapid reorientation about the crystalline c -axis. This is quite reasonable for a planar $\text{K}(\text{NH}_3)_4^+$ ion within the intercalation gallery [4]. The relative magnitudes of the ^1H - ^1H and ^{14}N - ^1H dipolar splittings show that the molecular geometry of the NH_3 is unchanged from that found in the gas. From the broadening of the outer satellites at angles other than 0° and 90° , they were able to measure the mosaic spread of the crystallites within the intercalated HOPG as about 3° , about a degree greater than that typical of pristine HOPG. From the detailed orientation dependence of the central lines, they determined the ^{14}N quadrupolar coupling constant as 3.7 MHz, intermediate between the gas value of 4.1 MHz and the solid-state value of 3.2 MHz. From the difference in linewidth between the central line and that of its nearest satellites, attributable to the ^{14}N quadrupolar relaxation, they estimate the activation energy for motion of the NH_3 in the gallery as 0.15 eV. From the ^{13}C NMR spectra [5] of these alkali metal-ammonia GICs, they determined the isotropic and anisotropic parts of the chemical shift. The anisotropic component is a linear function of the square root of the charge transfer in other GICs, so the measurement in $\text{KC}_{24}(\text{NH}_3)_4$ enabled them to estimate that the effect of introducing the four NH_3 molecules into KC_{24} was to reduce the charge transferred by the K to the graphite by 16%.

Wein et al. [6,7] have examined the similar alkali metal-ammonia intercalates of various layered metal disulfides. The ^1H study was conducted with both ^{14}N and ^{15}N ammonia. As expected, the identification of the nitrogen-proton dipolar coupling was confirmed. The angular dependence of the spectra at room temperature shows that the C_3 axis of the NH_3 molecule is parallel to the sulfide planes, perpendicular to the crystalline c -axis, and that there is also reorientation about an axis parallel to the c -axis, just as was found in the similar graphite intercalation compounds. At low temperatures, the reorientation about the directions parallel to the c -axis can be frozen out. For $(\text{NH}_4)_x(\text{NH}_3)_y\text{MS}_2$, they see not only a T_1 minimum due to NH_3 reorientation, but also one at lower temperatures due to NH_4^+ reorientation. A recent study by O'Bannon et al. [8] on $(\text{NH}_4)_x(\text{NH}_3)_y\text{TiS}_2$ also found reorientation of the NH_3 about its C_3 axis, but attributed the splitting to planar NH_3 molecules. This conclusion should be re-examined in light of the excellent agreement found in other intercalation compounds with the normal pyramidal geometry of ammonia.

In a remarkable study, McDaniel et al. [9] used ^2H NMR to study the dynamics of perdeutero-pyridine intercalated in 2H-TaS_2 . Using a solid echo sequence, they were able to obtain the entire 300 kHz powder spectrum at low

temperatures and to follow the motional averaging of the three distinguishable deuteriums in pyridine as the temperature was increased. They found that the model supported by their data has the plane of the pyridine molecule perpendicular to the sulfide planes, the molecular C_2 -symmetry axis parallel to the sulfide planes, and the averaging motion a reorientation about an axis parallel to the crystalline c -axis. A similar study by Jonas et al. [10] at Illinois showed the same pyridine orientation and same pyridine reorientation in $CdPS_3$. This is in contrast to the earlier conclusion of the Michigan group of Lifshitz et al. [11], based on their 2H single crystal study of the same compound, that the plane of the pyridine molecule was parallel to the sulfide layers and perpendicular to the c -axis. Both studies agreed that the motional averaging was due to reorientation about an axis parallel to the crystalline c -axis, but the work of Jonas et al. appears to account for all the spectral features and their temperature dependence. The Michigan group [12] has also used ESR to study the intercalation of the $CdPS_3$ host lattice with pyridine complexes of Mn^{2+} and has shown that Cd^{2+} can be displaced from the host lattice by Mn^{2+} .

NMR studies of tetrahydrofuran (THF) intercalated into alkali metal GICs have yielded information on the orientation of the THF and on its mobility. Goldmann et al. [13] find that the stage-two compound $Cs(THF)_{1.05}C_{24}$ has rigid THF molecules at 200 K with the THF molecules lying parallel to the graphene layers. At room temperature, the 1H line has narrowed somewhat and the most probable motion is a pseudorotation of the molecule with a fixed dipolar axis. In contrast, the first stage $Cs(THF)_{1.7}C_{24}$ compound has 50% of the THF molecules rigid at 295 K and 50% rotating freely about the crystalline c -axis. The ^{13}C study of these compounds by Quinton et al. [14] found the same chemical shift as for the $K(NH_3)_{4.3}C_{24}$ compound studied by Resing's group at NRL [5], so the effect of the THF intercalant appears to be very similar to that of NH_3 for the alkali metal GICs.

Some interesting NMR studies have been done on binary intercalation compounds of the clay, kaolinite, $Al_2(OH)_4Si_2O_5$, which is a more complex layered host lattice than graphite or the metal sulfides. Raupach et al. [15] examined three closely related intercalation compounds of kaolinite with dimethylselenoxide (DMSeO) using ^{77}Se and ^{13}C NMR. The three intercalation compounds have d -spacings of 10.95, 11.26 and 11.38 Å, with the $d = 11.26$ Å compound structurally analogous to the previously studied dimethylsulfoxide (DMSO) intercalation compound of kaolinite [16,17]. The ^{77}Se NMR spectrum shows only a single kind of Se present. The two methyl groups within the molecule are not equivalent, however, either in the DMSeO or in the DMSO intercalation compound. The two methyl groups show different ^{13}C chemical shifts and different T_1 's. The structural studies show one of the two methyl groups is keyed into a ditrigonal cavity of the kaolinite. The Lipsicas group [16] also studied kaolinite intercalates with formamide and N -methylformamide. An ^{27}Al NMR study of the hydroxy-aluminum pillared clay, beidellite,

and the pillaring solutions was done by Schutz et al. [18], using magic angle spinning to examine the clay. A ^1H NMR study [19] of H_2O in double-metal layered hydroxides, $\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2(\text{NO}_3)_x \cdot n\text{H}_2\text{O}$, found that the H_2O was oriented with its H-H vector aligned along the crystalline c -axis.

Kauzlarich et al. [20] undertook the challenging task of studying intercalation compounds of tetrathiafulvalene (TTF) and similar tetrasulfur compounds intercalated into the layered FeOCl host lattice. The ^1H NMR spectrum of the $\text{FeOCl}(\text{TTF})_{1/8.5}$ compound is a nearly featureless line extending over 1000 ppm. Large effects are expected from the unpaired electron spins and, indeed, no ^{13}C CPMAS spectra could be obtained from this compound.

A more classical study was that of Karunanithy et al. [21] who used ^{19}F NMR to study $\text{C}_7\text{SO}_3\text{F}$ (stage 1). Using the NMR technique developed by Resing and coworkers [22], they determined the conductivity of the material. As in the AsF_5 GICs [3b], there is a stage-dependent chemical shift which they were able to characterize well. A related study by the Vancouver group [23] involved the more complex halogen (III) fluorosulfates and their derivatives in fluorosulfuric acid as a solvent. The ^{19}F lines are appreciably broader and the spectra are not as informative as those of the simpler fluorosulfate intercalation compounds. Ebert et al. [24] discuss the NMR studies of the much-studied C_7SbF_5 and $\text{C}_{10}\text{AsF}_5$ GICs and conclude that the behavior of these systems is more complicated than that expected from a simple mixture of MF_6^- and MF_3 ($\text{M} = \text{Sb}, \text{As}$), which is indeed the case [3].

Touhara et al. [25] have begun a study of the stage 2 graphite intercalation compound of fluorine, $\text{C}_{6.3}\text{F}$, and of the mixed stage ($n=1$ and $n=2$) $\text{C}_{5.6}\text{F}$ compound. This system is tricky, because HF is usually needed to make the intercalation take place and we found (unpublished work, Resing and Miller) some preparations with substantial HF present. Touhara et al. find a linewidth transition in the ^{19}F spectrum at about 150 K for both $\text{C}_{6.4}\text{F}$ and stage 2 C_xHF_2 , and promise further work on these systems.

The ternary compound $\text{KH}_{2/3}\text{C}_8$ continues to be a much studied system. The hydrogen forms a layer between two layers of potassium in the intercalation galleries of this stage two compound. Kume and coworkers provide NMR and ESR evidence for a metallic character for the hydrogen [26,27]. Miyajima and coworkers [28] find the ^1H line inhomogeneously broadened (40 kHz, FWHM) below 77 K, but with the intrinsic linewidth of the spin isochromat about 3.6 kHz. The inhomogeneous broadening may be connected with possible Fe impurities in the Grafoil used to prepare their sample. An ESR study of C_{4n}KH_x ($n=1,2$; $x \sim 0.8$) by Enoki et al. [29] shows that the temperature dependence of the diffusion time is associated not only with the conduction-electron spins, but also with localized spins, attributed to association of electrons with defects caused by hydrogen deficiency.

Conard et al. [30] utilized ^{13}C NMR to study the HNO_3 and SbCl_5 GICs and the commensurate-incommensurate transition. Lauginie [31] has reviewed

band models and experimental measurements for alkali metal GICs and concludes that NMR and photoelectron spectroscopy results agree in showing the major role of pi-states in the vicinity of the Fermi level. The theoretical treatment of carbon in GICs continues to be of interest, with calculations of ^{13}C chemical shifts from Saito et al. [32,33] and Tsang and Resing [34,5].

In the realm of new techniques, the use of beta radiation-detected NMR of ^8Li in LiC_6 offers very high sensitivity due to the high polarization achieved by irradiation of ^7Li by polarized neutrons rather than the usual thermal Boltzmann distribution between spin levels. Heitjans and coworkers [35,36] have studied the diffusion of lithium from 250–700 K. There is a T_1 minimum near 400 K. From 600 K to the transition to the disordered phase at 715 K there is a quadrupolar interaction contributing to T_1 which may be due to correlated multiple-vacancy diffusion.

The intercalation of metallocenes into layered metal sulfides presents interesting problems, since these molecules are nearly spherical. Heyes et al. [37] report in a preliminary note the use ^2H NMR to show that at 300 K roughly half the cobaltocenium ions intercalated into 2H-TaS_2 are oriented with their C_5 -axes along the crystalline c -axis and the other half of the cobaltocenium ions are oriented with their C_5 -axes perpendicular to c . At 300 K, cobaltocenium ions in both orientations are rotating fast around an axis parallel to the c -axis, giving rise to a superposition of two powder patterns. (In pure metallocenes, rapid reorientation about the C_5 -axis is found at room temperature; cobaltocenium ion in the orientation with C_5 perpendicular to c is undergoing fast reorientation about two perpendicular axes.) At 200 K, a single powder pattern is found, characteristic of only fast internal reorientation about C_5 . The intensity changes found suggest that the cobaltocenium ions with their C_5 -axes perpendicular to c at room temperature may reorient at lower temperatures to be parallel to c . Lifshitz et al. [38] use ESR to study the orientation of cobaltocene, nickelocene and chromocene intercalated into $\text{Cd}_2\text{P}_2\text{S}_6$. Both neutral cobaltocene and the nickelocenium cation are oriented with the C_5 -axis parallel to the crystalline c -axis, while the orientation of the chromocenium cation is such that the C_5 -axis is perpendicular to c .

In contrast to the relatively weak interactions between the host lattice and the metallocenes, ESR shows that the fluorine of OsF_6^- interacts strongly with the carbon in the OsF_6 GICs [39]. Only 38% of the holes on the graphene planes are free, while the rest are involved in partial covalent bonds with the fluorine. For the OsF_6 GIC, the charge transfer is 1 electron per intercalant, while for the similar MoF_6 GIC, the transfer is only about 0.2 electron per intercalant, leaving most of the MoF_6 as neutral molecules in the van der Waals gap. HOPG intercalated with OsF_6 was used to study [40] the anisotropy of the g -factor and to determine the zero-field splitting parameter, D . The variation of D with stage indicates that the charge distribution around the intercalant species changes in going from stage one to stage two.

The study of charge carrier spin resonance (CCSR) is aided by the careful consideration of sample geometry, sample orientation in the ESR cavity, and modulation frequency for conducting samples. This subject has received renewed attention from Walmsley et al. [41], and by Blinowski and coworkers [42,43], based on Dyson's theory [44]. Rolla and coworkers [45,46] used the CCSR hysteresis to study the kinetics of ordering near the transition temperatures in SbCl_5 -intercalated graphite and AlCl_3 -intercalated graphite. Walmsley et al. [47] used the CCSR to extract the absolute value of the *c*-axis resistivity in the SbCl_5 GIC. Vaknin et al. [48] do both conductivity and ESR studies of HOPG intercalated with fluorine, showing that more careful treatment is required for GICs. They extract an activation energy for conduction hopping from the temperature dependence of the *c*-axis conductivity. The interest in lithium containing materials of possible use for high energy density batteries has prompted an ESR study [49] of lithium intercalates of FePS_3 , where reduced Fe in the border domains gives rise to an ESR signal, but no ESR line is observed for the main Fe, presumably because of a very short T_1 .

Palchan et al. [50] used ESR to measure the kinetics of intercalation of HNO_3 into HOPG. Dramatic changes are seen as soon as the sample is exposed to HNO_3 vapor, whether at low pressure (80 Torr) or high (300 Torr). By fitting the lineshape data, they were able to determine the diffusion constant as $D = (4.4 \pm 2.2) \cdot 10^{-7} \text{ cm}^2 \text{ min}^{-1}$. Davidov et al. [51] have used pulsed ESR to study the AsF_5 GIC and the $\text{BF}_3 + \text{F}_2$ GIC compounds made with HOPG. The FID T_2^* times are almost isotropic and are consistent with the CW observed linewidths. Neither the pulsed nor the CW studies find any significant anomalies in the AsF_5 GIC at 140 K, the temperature at which there is other evidence for an order-disorder phase transition for the intercalant. At temperatures below 20 K, a Hahn echo is observed, strongly suggesting that a small percentage of the electron spins are localized.

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REFERENCES

- 1 T. Tsang, R.M. Fronko, H.A. Resing, X.W. Qian and S.A. Solin, *Solid State Commun.*, 63 (1987) 361.
- 2 T. Tsang, R.M. Fronko and H.A. Resing, *J. Magn. Reson.*, 72 (1987) 315.
- 3 (a) G.R. Miller, M.J. Moran, H.A. Resing and T. Tsang, *Langmuir*, 2 (1986) 194;
(b) M.J. Moran, G.R. Miller, R.A. DeMarco, H.A. Resing, *J. Phys. Chem.*, 88 (1984) 1580.
- 4 H.A. Resing, R.M. Fronko, T. Tsang and S.A. Solin, *Synth. Met.*, 23 (1988) 297.
- 5 T. Tsang, R.M. Fronko, H.A. Resing, X.W. Qian and S.A. Solin, *Solid State Commun.*, 62 (1987) 117.
- 6 E. Wein, W. Müller-Warmuth and R. Schöllhorn, *Solid State Ionics*, 22 (1987) 231.
- 7 E. Wein, W. Müller-Warmuth and R. Schöllhorn, *Z. Phys. Chem. (Munich)*, 15 (1987) 113.
- 8 G.W. O'Bannon, W.S. Glaunsinger and R.F. Marzke, *Solid State Ionics*, 26 (1988), 15.
- 9 P.L. McDaniel, T.M. Barbara and J. Jonas, *J. Phys. Chem.*, 92 (1988) 626.
- 10 P.L. McDaniel, G. Liu and J. Jonas, *J. Phys. Chem.*, 92 (1988) 5055.
- 11 E. Lifshitz, S. Vega, Z. Luz, A.H. Francis and H. Zimmermann, *J. Phys. Chem. Solids*, 47 (1986) 1045.
- 12 D.A. Cleary, J. Groh, E. Lifshitz and A.H. Francis, *J. Phys. Chem.*, 92 (1988) 551.
- 13 M. Goldmann, A.J. Dianoux, B. Gonzalez, F. Beguin, H. Estrade-Szwarckopf and J. Conard, *Synth. Met.*, 23 (1988) 55.
- 14 M.F. Quinton, A.P. LeGrand, L. Facchini and F. Beguin, *Synth. Met.*, 23 (1988) 271.
- 15 M. Raupach, P.F. Barron and J.G. Thompson, *Clays Clay Miner.*, 35 (1987) 208.
- 16 J.G. Thompson and C. Cuff, *Clays Clay Miner.*, 33 (1985) 490.
- 17 M. Lipsicas, R. Raythatha, R.F. Giese Jr and P.M. Costanzo, *Clays Clay Miner.*, 34 (1986) 635.
- 18 A. Schutz, W.E.E. Stone, G. Poncelet and J.J. Fripiat, *Clays Clay Miner.*, 35 (1987) 251.
- 19 G. Marcelin, N.J. Stockhausen, J.F.M. Post and A. Schutz, *J. Phys. Chem.*, 93 (1989) 4646.
- 20 S.M. Kauzlarich, J.F. Ellena, P.D. Stupik, W.M. Reiff, B.A. Averill, *J. Am. Chem. Soc.*, 109 (1987) 4561.
- 21 S. Karunanithy, J.M. Willis and F. Aubke, *Synth. Met.*, 24 (1988) 379.
- 22 H.A. Resing, M.J. Moran and G.R. Miller, *J. Chem. Phys.*, 76 (1982) 1706.
- 23 M.S.R. Cader, S. Karunanithy and F. Aubke, *Synth. Met.*, 30 (1989) 9.
- 24 L.B. Ebert, A.R. Garcia and H. Selig, *Rev. Chim. Miner.*, 23 (1986) 543.
- 25 H. Touhara, Y. Goto, N. Watanabe, K. Imaeda, T. Enoki, H. Inokuchi and Y. Mizutani, *Synth. Met.*, 23 (1988) 461.
- 26 K. Nomura, T. Saito, K. Kume and H. Suematsu, *Solid State Commun.*, 63 (1987) 1059.
- 27 T. Saito, K. Nomura, K. Mizoguchi, K. Mizuno, K. Kume and H. Suematsu, *J. Phys. Soc. Jpn.*, 58 (1989) 269.
- 28 S. Miyajima, T. Chiba, T. Enoki, H. Inokuchi and M. Sano, *Phys. Rev. B*, 37 (1988) 3246.
- 29 T. Enoki, H. Inokuchi and M. Sano, *Phys. Rev. B*, 37 (1988) 9163.
- 30 J. Conard, H. Fuzellier and R. Vangelisti, *Synth. Met.*, 23 (1988) 277.
- 31 P. Lauginie, *Synth. Met.*, 23 (1988) 311.
- 32 R. Saito, K. Kobayashi, M. Tsukada and H. Kamimura, *Synth. Met.*, 23 (1988) 291.
- 33 R. Saito, M. Tsukada, K. Kobayashi and H. Kamimura, *Phys. Rev. B*, 35 (1987) 2963.
- 34 T. Tsang and H.A. Resing, *Solid State Commun.*, 53 (1985) 39.
- 35 P. Heitjans, *Synth. Met.*, 23 (1988) 257.
- 36 P. Freiländer, P. Heitjans, H. Ackermann, B. Bader, G. Kiese, A. Schirmer H.-J. Stöckmann, C. Van der Marel, A. Magerl and H. Zabel, *Z. Phys. Chem. (Munich)*, 151 (1987) 93.
- 37 S.J. Heyes, N.J. Clayden, C.M. Dobson, M.L.H. Green and P.J. Wiseman, *J. Chem. Soc., Chem. Commun.*, (1987) 1560.
- 38 E. Lifshitz, D.A. Cleary and A.H. Francis, *Chem. Phys.*, 127 (1988) 305.

- 39 I. Ohana, D. Vaknin, H. Selig, Y. Yacoby and D. Davidov, *Phys. Rev. B*, 35 (1987) 4522.
- 40 D. Vaknin, D. Davidov, V. Zevin and H. Selig, *Phys. Rev. B*, 35 (1987) 6423.
- 41 L. Walmsley, G. Ceotto, J.H. Castilho and C. Rettori, *Synth. Met.*, 30 (1989) 97.
- 42 J. Blinowski, P. Kacman, C. Rigaux and M. Saint-Jean, *Synth. Met.*, 12 (1985) 419.
- 43 M. Saint-Jean, C. Rigaux, J. Blinowski, B. Clerjaud, P. Kacman and G. Furdin, *Ann. Phys. (Paris)*, 11 (1986) 215.
- 44 F.J. Dyson, *Phys. Rev.*, 98 (1955) 349.
- 45 S. Rolla, L. Walmsley, H. Suematsu and C. Rettori, *Phys. Rev. B*, 36 (1987) 2893.
- 46 S. Rolla, L.C. Walmsley and C. Rettori, *Synth. Met.*, 23 (1988) 43.
- 47 L. Walmsley, S. Rolla and C. Rettori, *Synth. Met.*, 23 (1988) 305.
- 48 D. Vaknin, I. Palchan, D. Davidov, H. Selig and D. Moses, *Synth. Met.*, 16 (1986) 349.
- 49 P. Colombet, G. Ouvrard, O. Anstson and R. Brec, *J. Magn. Magn. Mater.*, 71 (1987) 100.
- 50 I. Palchan, D. Davidov, V. Zevin, G. Polatsek and H. Selig, *Synth. Met.*, 16 (1986) 215.
- 51 D. Davidov, A. Grupp, H. Käss and P. Hoffer, *Synth. Met.*, 23 (1988) 291.