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VIBRATIONAL EXCITATIONS OF PURE $FeCl_3$ AND GRAPHITE INTERCALATED WITH FERRIC CHLORIDE[+]

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The polarized Raman spectra of crystalline $FeCl_3$, and of stage 1 and 2 graphite-$FeCl_3$ intercalation compounds have been obtained. The observed $FeCl_3$ derived modes are assigned vibrational species according to the space group C_{3i}^2 ($R\bar{3}$) for the pure crystal and the D_{3d} layer factor group for the intercalated compounds. Measurements show that $FeCl_3$ intercalated in graphite maintains its layer structure, no evidence for monomeric $FeCl_3$ or dimeric Fe_2Cl_6 being observed. There is also no evidence for $FeCl_2$ layer stochiometry.

It was first shown in 1932 by Thiele[1] that ferric chloride will intercalate graphite. Since that initial observation the ferric chloride intercalant has become one of the most heavily studied rivaling C_nM M = K, Rb, Cs and C_nBr for the sheer volume of independent investigations of which it has been the focus.[2] To date however there have been no studies of the vibrational excitations and lattice properties of graphite-$FeCl_3$. Such studies and particularly those carried out using the Raman spectroscopic technique have proved indispensable to the understanding of the physical properties of the alkali metal[3,4,5] and bromine intercalation compounds. As we shall now show such techniques are also fruitfully applied to graphite-$FeCl_3$.

As the result of an excellent electron diffraction and x-ray diffraction investigation of graphite-$FeCl_3$ by Cowley and Ibers[6] a great deal is known about the structure of graphite-$FeCl_3$ which is intrinsically interesting and somewhat unique. Consider first pure $FeCl_3$. It is, like graphite itself, a layer crystal but with the BiI_3 structure for which the hexagonal non-primitive unit cell consists of three layers each containing 2 $FeCl_3$ units.[7] A given layer in this structure is composed of a layer of iron atoms sandwiched halfway between two distinct layers of chlorine atoms in such a way that the iron atoms are octahedrally coordinated to six chlorine atoms with the three fold axis of the chlorine octahedra parallel to the c axis of the crystal. This layer structure and the layer primitive cell are shown in Fig. 1. Notice from Fig. 1 that the chlorine atoms within a layer form a triangular lattice whereas the iron atoms form the more open honeycomb structure identical in form to the layers in graphite. If the sites at the centers of the iron hexagons were also occupied the layer sandwiched would have $FeCl_2$ stoichiometry and the resultant three dimensional crystal would then have the $CdCl_2$ structure.[7]

One of the most intriguing things about the graphite-$FeCl_3$ system is that upon intercalation $FeCl_3$ enters the graphite planar interstices as layers with essentially the same structure that obtains in pure $FeCl_3$. In particular for the stage 1 compound $C_{6.6}FeCl_3$ the iron atoms form two dimensionally ordered domains of typical size 1000 Å and with an iron layer structure identical to that in pure $FeCl_3$.[6,8] However, the iron lattice is incommensurate with the graphite lattice the a axis lattice parameters being respectively 6.06 Å and 2.46 Å.[6] Therefore, the chlorine atoms tend to retain an undistorted octahedral coordination about the iron atoms identical to that in pure $FeCl_3$ and simultaneously occupy preferred sites associated with the carbon host. As a result of these competing conditions the chlorine atoms lose long range ($\approx$ 1000 Å) two dimensional order and randomly occupy the preferred sites. Nevertheless the distortions of the octahedra engendered by preferred site occupation are small ($\sim 3^\circ$ relative rotation of the chlorine triangles, 2'2'2' and 2 2 2 in the octahedron of Fig. 1a, about the c axis of the layer). Therefore in what follows we shall ignore the above mentioned distortions and assume that the intercalated $FeCl_3$ layers in graphite-$FeCl_3$ have the same structure as in pure $FeCl_3$.

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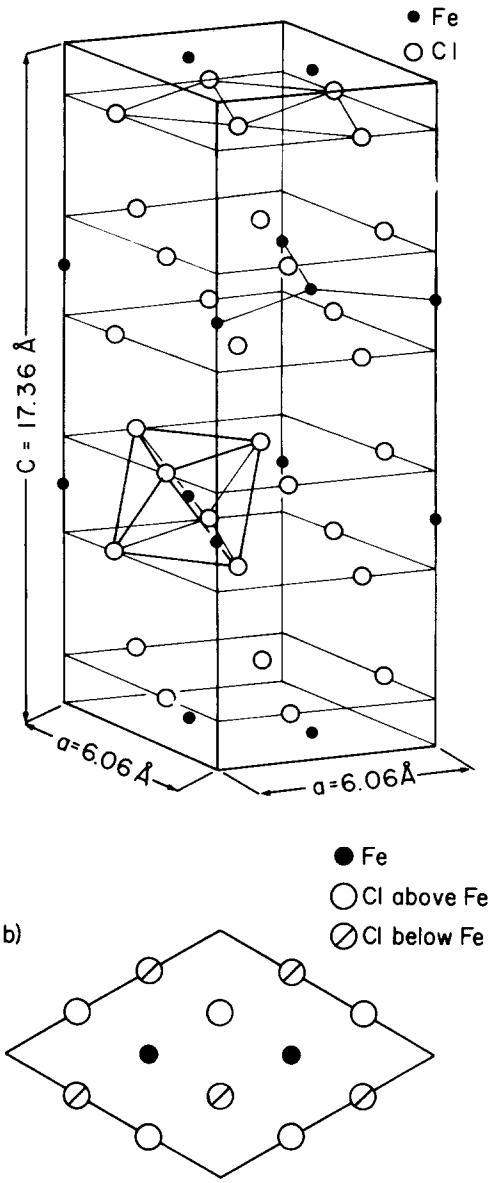

Fig. 1a The nonprimitive hexagonal C_{3i}^2 cell of $FeCl_3$. The intersection of each chlorine plane with the cell surface is indicated. Also shown is the triangular (6-fold coordinated) Cl plane structure, the hexagonal (3-fold coordinated) Fe plane structure, and an $FeCl_6$ octahedra.

Fig. 1b The D_{3d} primitive unit cell of an $FeCl_3$ sandwich layer viewed along the c axis normal to the layer. Relative sizes of chlorine and iron atoms are not to scale.

Samples of graphite $FeCl_3$ were prepared from anhydrous $FeCl_3$ and highly oriented pyrolytic graphite (HOPG) using the two zone method and vapor pressure isotherms reported by Hooley.[9] The sample stage was established from measurements of 00ℓ x-ray spectra which were made in situ, except as noted. X-ray measurements were made on a G.E. powder diffractometer using Mo Kα radiation. Raman spectra were recorded at room temperature in the backscattering configuration using 5145 Å or 4880 Å argon laser excitation.

An important point is to be made regarding sample homogeneity. A homogeneous stage 1 sample was not obtained even after prolonged heating at temperatures reported to produce homogeneous stage 1 in 200 mesh natural graphic flakes.[9] An 8 mm x 12 mm x .2 mm sample (dimensions before intercalation) heated for a total of 4 days showed x-ray lines of both "pure" stage 1 and HOPG. "Pure" is used here in the sense of Metz and Holwein[10] to denote uniform stage regions large enough to produce narrow ($\Delta 2\theta < .2^\circ$) x-ray reflections. The Raman spectra of this sample showed only stage 1 bands. The sample was then heated with T_{FeCl_3} = 400°C and $T_{graphite}$ = 410°C for one day. After this the x-ray spectrum indicated a pure stage 2 while Raman measurements indicated a 50-50 mixture of stage 2. An 8 mm x 6 mm x .2 mm sample had stage 1 and HOPG x-ray reflections and a stage 1 Raman spectra after being heated at stage 1 temperatures for 38 hrs. After 7 days both x-ray and Raman in situ measurements indicated pure stage 1. However when removed from its preparation tube and cleaved, the inside surface showed evidence of both stage 1 and HOPG in its Raman spectrum. X-ray reflections still indicated only stage 1.

We chose Mo Kα radiation to excite the x-ray spectra because the pyrex sample preparation tubes are relatively transparent at that energy. The "sampled depth" ($\approx 1/2$ the penetration depth) of Mo Kα radiation is $\approx$ .2 mm for stage 1 and stage 2 graphite $FeCl_3$. In contrast, other reported x-ray measurements of homogeneous compounds used Cr Kα[10] radiation. The "sampled depth" of this radiation is $\approx 2.5 \times 10^{-2}$ mm, making sample inhomogeneities much less apparent. The 5145 Å and 4880 Å light used for Raman measurements samples even less; approximately 3×10^{-6} mm. Because the Raman experiment samples very little depth along the c direction, it probes inhomogeneities primarily in the a direction. We report data on samples which are homogeneous pure stages to the limit of the penetration depth of visible radiation. Sample preparation and homogeneity will be addressed in more detail elsewhere.[11]

Pure $FeCl_3$ crystals were prepared by vapor

transport during the intercalation process and grew at the cooler end of the sealed evacuated pyrex tube. The crystals of typical dimensions 3 mm x 3 mm x .5 mm exhibited a clearly defined hexagonal morphology and dark green mirrorlike surfaces. They too were studied in situ, a necessity given the extremely hygroscopic character of $FeCl_3$.

Polarized Raman spectra of both graphite-$FeCl_3$ and pure $FeCl_3$ were recorded at room temperature and were excited with the 4880 Å and 5145 Å argon laser excitation lines using the back scattering geometry. Since stages 1 and 2 graphite $FeCl_3$ and $FeCl_3$ itself are uniaxial layer materials the group theoretical symmetry species of their vibrational excitations could be determined with incident radiation propagating along the "c" axis irrespective of the orientation of the a axis.

As noted above, $FeCl_3$ crystallizes in the BiI_3 structure and has space group symmetry C_{3i}^2 $(R\bar{3})$ with 2 molecular units in the rhombohedral primitive cell.[7] Its vibrational excitations transform according to the irreducible representations

$$\Gamma_{vib.}^{cryst.} = 4\,A_g + 3\,A_u + 4\,E_g + 3\,E_u \ .$$

The $4\,A_g + 4\,E_g$ modes are Raman active while the $3\,A_u + 3\,E_u$ modes are infrared active.

Consider also the $FeCl_3$ layers from which the three dimensional structure is built up. As can be seen from Fig. 1 the layer has factor group symmetry D_{3d} and its primitive cell also contains two $FeCl_3$ units. The vibrational excitations of the layer transform according to the irreducible representations of the D_{3d} point group as follows:

$$\Gamma_{vib.}^{layer} = 2\,A_{1g} + 2\,A_{2g} + 4\,E_g + A_{1u} + 2\,A_{2u} + 3\,E_u \ .$$

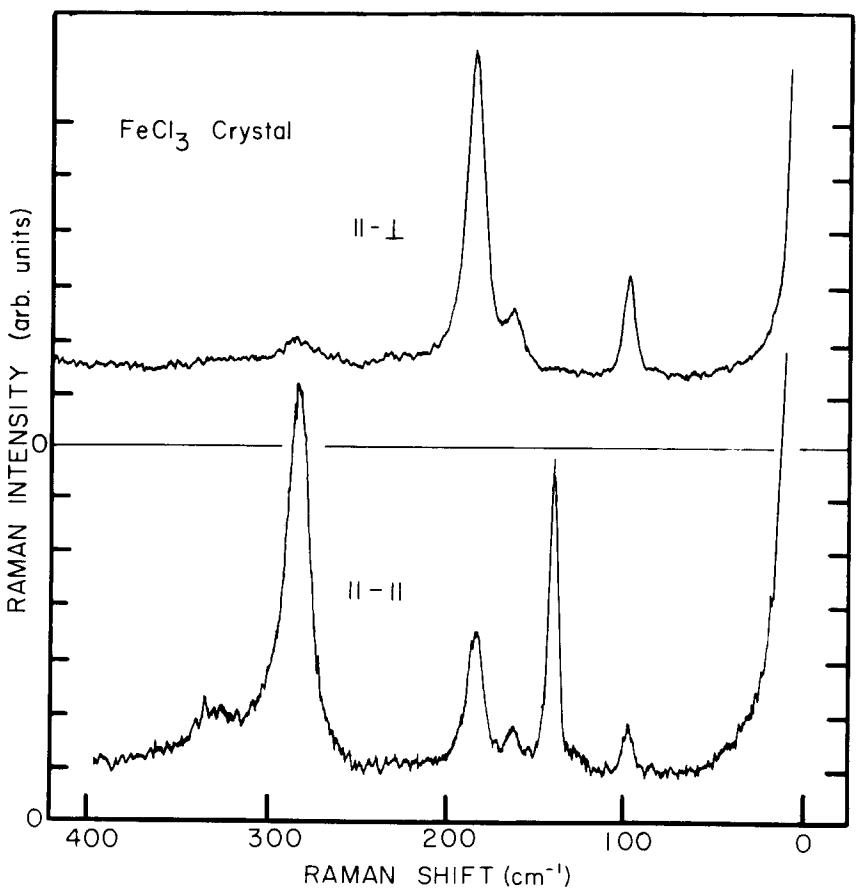

Fig. 2 The polarized Raman spectra of single crystal $FeCl_3$. The spectra were excited with 25 mw of 5145 Å argon laser radiation and recorded in the backscattering configuration using a spectral slit width 4.7 cm^{-1}. Note that the abscissa are linear in wavelength rather than wavenumber.

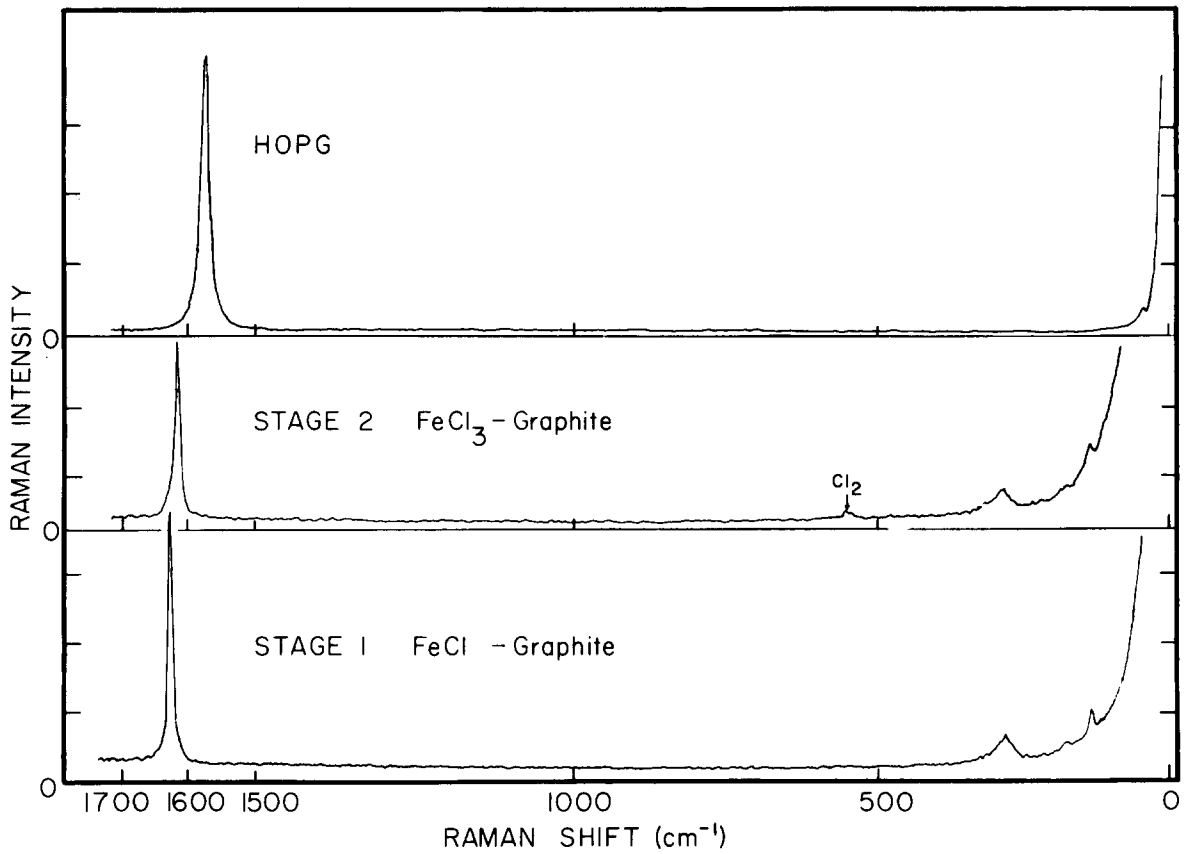

Fig. 3 The Raman spectra of stage 1 and stage 2 graphite $FeCl_3$ compared with the corresponding spectrum of pristine HOPG. The spectra were excited with 100 mw of 5145 Å argon laser radiation and recorded in the backscattering configuration using a spectral slit width 4.7 cm^{-1}. The feature of 555 cm^{-1} in the spectrum of the stage 2 compound is due to Cl_2 vapor which was introduced at a pressure of 1 atom prior to sealing off and heating the sample tube. Note that the abscissa are linear in wavelength rather than wavenumber.

Of these 2 A_{1g} + 4 E_g or six modes are Raman active. Note that both the A_{1g} and A_{2g} excitations of the layer correlate to the A_g modes of the crystal whereas the E_g layer modes correlate to the E_g crystal modes.

In Figs. 2(a) and (b) we show the polarized Raman spectra of pure $FeCl_3$ single crystals. The spectrum labelled ||, || will contain both A_{1g} and E_g modes whereas that labeled ||, ⊥ will contain only the E_g modes. This distinction results from the structure of the Raman tensors for A_{1g} and E_g of C_{3i} and the fact that the former which contains no off diagonal elements is invariant under rotations about the optic axis. Six of the eight group theoretically predicted modes of $FeCl_3$ are observed and their positions and symmetry species are labeled in Table 1. By comparison with the spectra of other crystals with the BiI_3 structure[12] the weak mode at 341 cm^{-1} is identified as having A_{1g} symmetry but this designation is somewhat uncertain.

The Raman spectra of graphite $FeCl_3$ may be divided into two regions: a high frequency region consisting of graphite intralayer modes and a lower frequency region consisting of intercalant modes.

Fig. 3 shows the complete spectra of stage 1 and stage 2 graphite $FeCl_3$ and pristine HOPG. We will concentrate first on the high frequency region. As expected from the nearest layer model of Nemanich, Solin and Guerard[3] the samples show a single sharp depolarized band in this region. This band is associated with the E_{2g_2} 1580 cm^{-1} intralayer mode of the hexa-

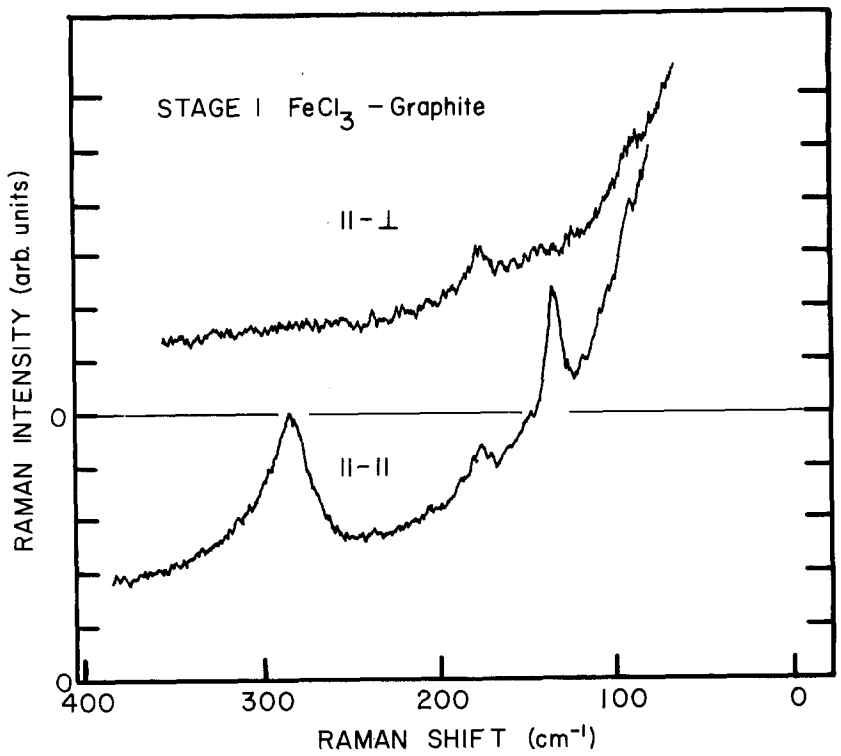

Fig. 4 The polarized Raman spectra of the intercalant intralayer modes of stage 1 graphite $FeCl_3$. The spectrum of stage 2 graphite $FeCl_3$ is identical except for a scale factor due to smaller concentration. The spectra were excited with 100 mw of 5145 Å argon laser radiation and recorded in the backscattering configuration using a spectral slit width 4.7 cm^{-1}. Note that the abscissa are linear in wavelength rather than wavenumber.

gonal graphite network.[13,14,3] For a stage 1 compound in which each graphite layer is flanked on both sides by $FeCl_3$ layers, the mode is upshifted from the corresponding vibration of pristine graphite [13,14] by 46 cm^{-1} to 1626 cm^{-1}. Similarly the stage 2 compound in which each graphite layer is flanked by one graphite and one $FeCl_3$ layer exhibits a high frequency mode upshifted by 32 cm^{-1} to 1612 cm^{-1}.

Figure 4 shows the polarized Raman spectra of the low frequency ($\omega < 400$ cm^{-1}) region. All samples examined, including those of mixed stage, show identical structure in this region. Four bands are observed one, with maximum intensity at 287 cm^{-1}, being quite broad and asymmetric. These bands are clearly intralayer modes of the intercalated $FeCl_3$ layer. Stage 1 and stage 2 therefore have the same $FeCl_3$ layer structure. Our assumption that the optical vibrational spectra of graphite $FeCl_3$ can be analyzed by treating the $FeCl_3$ layers as structurally identical to those in pure $FeCl_3$ is borne out by the spectra of Fig. 4. For instances one expects 2 A_{1g} modes for the intercalant layer excitations. We observe both at 139 cm^{-1} and 287 cm^{-1} in the intercalated compound. Moreover, those two modes, although slightly shifted by ≈ 5 cm^{-1} clearly correspond to layer excitations in pure $FeCl_3$. Two of the four group theoretically predicted E_g modes are also observed. These too correspond to and are downshifted from modes of pure $FeCl_3$.

It can be seen from the spectra of Figs. 2 and 4 that the spectral features of the intercalant are somewhat broadened relative to the corresponding features in pure $FeCl_3$. This broadening which is not of instrumental origin is especially noticeable for the A_{1g} mode at 287 cm^{-1} and is probably a manifestation of the disorder associated with the Cl atoms which participate in both A_{1g} modes and three of the four E_g modes of the intercalant layer.

Some of the $FeCl_3$ intercalate literature addresses the question of $FeCl_2$ content. Hooley has suggested on

TABLE I

Energy shifts in cm^{-1} and symmetry species of the Raman bands of graphite, $FeCl_3$, and graphite-$FeCl_3$

Pristine HOPG (D^4_{6h})	Pristine $FeCl_3$ (C^2_{3i})	stage 1 graphite $FeCl_3$ (D^1_{3d})	stage 2 graphite $FeCl_3$ (D^1_{3d})
47 (E_{2g_1})[a]			
	98 (E_g)	93 (E_g)	
	142 (A_g)	139 (A_{1g})	139 (A_{1g})
	164 (E_g)		
	186 (E_g)	181 (E_g)	181 (E_g)
	282 (A_g)	287 (A_{1g})	287 (A_{1g})
	354 ($A_{g?}$)		
1580 (E_{2g_2})		1626 (E_{2g_2})	1612 (E_{2g_2})

[a] See Ref. 15.

the basis of Mossbauer studies that at low temperature 3% of the iron in the stage 1 compound is in a 2^+ state.[15] There is no evidence in our Raman spectra for $FeCl_2$ layer excitations which would have $\Gamma^{vib.}_{layer} = A_{1g} + E_g$ and based on the spectra of $FeCl_2$ crystals would occur at $\approx 149\ cm^{-1}$ and $250\ cm^{-1}$ respectively.[16] Moreover, our Raman results not only clearly confirm that $FeCl_3$ occupies the graphite lattice as layers but we see no evidence for monomeric $FeCl_3$ or dimeric Fe_2Cl_6 which are prominent components of the vapor produced during the intercalation process. The Raman spectrum of monomeric $FeCl_3$ which has symmetry C_{3v} contains as expected two polarized and two depolarized bands which occur at 69 (A_1), 114 (E), 367 (A_1), and 460 cm^{-1} (E).[17] The spectra of Fe_2Cl_6 contains additional features but its most intense bands correspond to those of $FeCl_3$.[18] Thus the Raman spectra of $FeCl_3$ and Fe_2Cl_6 molecules are sufficiently distinct from the spectra we observe for the intercalation compounds that we conclude molecular forms of $FeCl_3$ if present constitute less than 1% of the intercalated species.

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