

Neutron Scattering Experiments on Well-Stage Graphite - FeCl<sub>3</sub>

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Introduction

This paper reports results of a neutron diffraction study on both the magnetic and the lattice dynamic structure of graphite-FeCl<sub>3</sub>. The FeCl<sub>3</sub> system was selected for this study because of the interesting magnetic properties previously reported for this system.<sup>1,2,3</sup> Of particular interest is the low temperature magnetic phase transition, which has been shown to be stage dependent.<sup>2,3</sup> For example, in the magnetic state, the spin alignment<sup>1</sup> has been reported to be in-plane with an assumption that within a single layer the spins were ferromagnetically aligned, but between planes the alignment could be either ferro (stage 2) or anti-ferromagnetic (stage 1). In addition, Mössbauer experiments<sup>2,3</sup> suggested that the stage 1 and 2 compounds showed very similar magnetic behavior<sup>3</sup>, while the stage 4 and 6 compounds failed to show a low temperature in-plane spin alignment.

Special emphasis was given to the study of the low temperature magnetic state of the Fe<sup>3+</sup> spins and to the longitudinal phonon modes for k<sub>z</sub> axis acoustic branches. All experiments reported here were carried out on a stage 2 sample of graphite-FeCl<sub>3</sub>. The sample was prepared by a two-zone vapor growth technique<sup>4</sup> and was characterized by (00l) x-ray and neutron diffraction patterns to be > 95% stage 2, with only minor inclusions of other stages.

Magnetic State

The results of the (00l) neutron scans for temperatures T > 80 mK showed no evidence for ferromagnetic spin alignment (either inter-planar or intra-planar) in a stage 2 compound. Static in-plane magnetic fields of up to ~6 Tesla were applied and fields of this magnitude failed to achieve ferromagnetic in-plane alignment by means of a spin flop transition. In this in-plane high field experiment at T ~0.1 K we were able to produce an in-plane magnetization which was only about 10% of the expected ferromagnetic saturation value. Some evidence of inter-planar magnetic correlations was however found. A weak (hk0) peak indicating a doubling of the in-plane unit cell was observed. However, from our analysis of the data we conclude that neither a ferro nor a simple 2 sublattice antiferromagnetic inter-planar alignment was compatible with our observations. The magnetic state inferred from the Mössbauer experiments<sup>3</sup> cannot definitively establish long-range order. A Mössbauer experiment is sensitive to the local spin environment and often is unable to distinguish a long-range ordering from a slowing down of a spin relaxation process.

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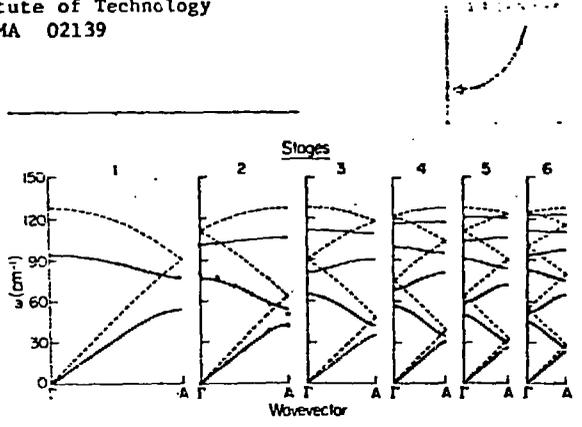


Fig. 1. Longitudinal phonon modes propagating in the z direction in graphite-FeCl<sub>3</sub> intercalation compounds. The dashed curve represents the zone folding of the pristine graphite branch. The points for stage 2 represent our inelastic neutron scattering measurements. The solid curves are calculated from the one-dimensional model discussed in the text.

These neutron diffraction results for our stage 2 sample are thus inconsistent with any of the previously proposed magnetic structures.<sup>1,3</sup> Though the results do not preclude a low temperature magnetic phase transition, neither do they confirm a conventional transition to a magnetically ordered state.

Lattice Modes

On the other hand, inelastic neutron diffraction peaks were observed in room temperature (00i) k-space scans. These diffraction peaks were identified with the longitudinal acoustic branches. Only 3 branches were observed and these are shown in the stage 2 panel of Fig. 1 as the open circles. The high frequency optical branch (which occurs at ~868 cm<sup>-1</sup> in pristine graphite) was not observed, nor were any of the FeCl<sub>3</sub> type intercalate vibrations observed. These intercalate FeCl<sub>3</sub> modes are expected to be IR-active and should occur in the 200 < ω < 500 cm<sup>-1</sup> range.<sup>5</sup>

The calculated results for the low frequency longitudinal phonon branches for stage 1 to 6 graphite-FeCl<sub>3</sub> are shown in Fig. 1, in which the dashed curve is the folded graphitic longitudinal mode and the solid curves are the result of a one-dimensional model calculation with nearest neighbor elastic interactions. The calculation of these branches as a function of stage is achieved by introducing additional graphite layers into the c-axis unit cell and using the same basic set of force constants (see Table 1). Because of the assumption that the interactions between graphite interior layers are identical

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to those in pristine graphite, we see that the higher stage compounds more nearly approximate the zone-folded pristine graphite result (dashed curve). Nevertheless, the intercalation compounds have more nearly dispersionless modes for the optic branches than is the case for pristine graphite.

The results for the longitudinal acoustic branches shown in Fig. 1 provide a critical test of any three dimensional lattice mode model for intercalated graphite. One such recently proposed model<sup>6</sup> was based on the known dynamical matrix for pristine graphite and incorporated  $k_z$ -axis zone-folding as imposed by the staging periodicity. The transverse coupling between the intercalate and graphite bounding layers was determined from Raman scattering experiments for the  $E_{2g}$  modes at  $\sim 1600 \text{ cm}^{-1}$  for both donor and acceptor compounds. The longitudinal coupling was assumed to be unchanged from that in pristine graphite<sup>6</sup> since no neutron scattering data were used in the parameter determination for the model. This three dimensional model<sup>6</sup> is in general agreement with the present experiment, but it fails in its simplest form to provide a detailed fit to the experimental data achieved by the one-dimensional model in Fig. 1. Therefore a one-dimensional model was constructed to interpret the measurements of the longitudinal acoustic branches and to provide force constant parameters (see Table 1) which will serve as input into a more general three-dimensional calculation of the phonon dispersion curves.

The force constants listed in Table 1 indicate that the graphite-intercalate coupling is about 30% weaker than the normal interplanar graphite-graphite coupling. This result is in contrast to the alkali metal donor compounds<sup>7</sup> which show that the alkali metal ion is bound more strongly to the graphite bounding layer, a result which is also consistent with the electronic properties of alkali metal intercalation compounds. However, intercalation with both  $\text{FeCl}_3$  and  $\text{K}$  is shown to result in a decrease in the bonding between the graphite bounding and graphite interior layers. This result suggests that the binding of the graphite to the intercalate layer shifts the  $\pi$  orbitals toward the intercalate and thus weakens the bonding to the graphite interior layers. This shift in the  $\pi$ -bond charge distribution toward the intercalate layer is consistent with the (00L) x-ray analysis of Leung et al.<sup>8</sup>

More precise modeling of the lattice modes will require additional experimental input regarding the intercalate modes as well as refinements of the theoretical model.

In addition to inelastic neutron diffraction data, IR and Raman spectra on an a-face sample of intercalated graphite<sup>5</sup> could detect both the intercalate layer modes and the high frequency modes which are derived from the graphitic  $A_{2u}$  and  $B_{1g}$  modes at  $\sim 870 \text{ cm}^{-1}$ .

Because of the symmetry of the intercalated graphite, the dynamical matrix can be factored for wave vectors along the  $\Gamma A$  axis in the Brillouin zone. This factorization implies that there is no mixing of the longitudinal and transverse modes along this axis. Thus, the

experimental mode determination and the theoretical one-dimensional modeling given here have important implications on the more general three dimensional modeling which is necessary to obtain the higher frequency branches correctly.

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Table 1. Force constants<sup>(a)</sup> for the one-dimensional model<sup>(b)</sup> for longitudinal modes.

Stage	$\phi_{x-C_b}$	$\phi_{C_b-C_i}$	$\phi_{C_i-C_i}$
n=1	0.725	-	-
n=2	0.725	0.879	-
n>3	0.725	0.879	1.0

(a) All force constants  $\phi_{\alpha\beta}$  are normalized to graphite, and X denotes the intercalate while  $C_i$  and  $C_b$  refer respectively to the graphite interior and bounding layers.

(b) The masses are taken to correspond to the chemical formula  $C_{\xi n}FeCl_3$  and the in-plane density  $1/\xi$  was assumed to be constant ( $\xi = 6.6$ ), independent of stage number n.