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Inelastic neutron scattering from low-frequency (00*q*) longitudinal lattice modes in graphite-$SbCl_5$ intercalation compounds

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Results of inelastic neutron scattering experiments on a stage-2 and -4 graphite-$SbCl_5$ intercalation compound are reported. A one-dimensional Born—von Kármán model is applied to interpret the data. Comparison of the results for $SbCl_5$-intercalated graphite with other recently reported neutron data for intercalation compounds suggests systematic trends in the magnitudes of the interactions.

INTRODUCTION

Graphite intercalation compounds (GIC's) are formed by the periodic insertion of layers of the intercalant species into the host graphite material. These compounds provide a classic example of the use of Brillouin-zone folding to account for superlattice effects on phonon dispersion relations. The ability to form well-staged graphite-$SbCl_5$ compounds[1] provides the framework to test a lattice-dynamical model for zone folding. For this system, a theoretical model with a unique set of force constants can be used to generate a complete sequence of low-frequency longitudinal lattice modes for all stages. This paper reports inelastic-neutron-scattering results in both stage-2 and -4 graphite-$SbCl_5$ compounds. The analysis of the results provides a stringent test of the lattice-dynamical model[2] for the most dilute acceptor compound yet measured by neutron spectroscopy.

The zone-folding model is successful in explaining the low-frequency (00*q*) longitudinal modes without explicitly accounting for the internal structure of the intercalate layer or for the known in-plane commensurate layer ordering in the graphite-$SbCl_5$ system.[3] The in-plane ordering is not expected to have a significant effect on the longitudinal modes reported here.

Inelastic neutron scattering on graphite intercalation compounds has recently provided a great deal of new structural and dynamical information about intercalation compounds.[4–9] The early neutron scattering experiments on pristine graphite by Nicklow, Wakabayashi, and Smith already demonstrated,[10] even without large single crystals of graphite, that low-frequency lattice modes could be resolved using highly oriented pyrolitic graphite (HOPG). Since HOPG (Ref. 11) is the basic host material for many recent studies on graphite intercalation compounds, it is anticipated that inelastic-neutron-scattering studies on HOPG-based intercalated samples will yield important structural and dynamical information about GIC's.

The alkali-metal (Li, K, Rb, and Cs) -intercalated graphite compounds have been investigated by a number of recent neutron scattering experiments[4–8] in which longitudinal modes propagating along the hexagonal axis have been measured for stage-1, -2, and -3 compounds. Although scattering experiments for in-plane wave vectors are somewhat more difficult to perform because of the polycrystalline nature of HOPG-based compounds, Kamitakahara *et al.*[6] have recently shown that the extreme in-plane anisotropy of the stage-2 graphite-Rb system makes it possible to obtain reasonably sharp structure for in-plane—mode neutron scattering scans, even for cylindrically averaged scattering vectors. The earlier work of Nicklow *et al.* on pristine graphite[10] also determined these basal-plane modes from inelastic scattering experiments, and used these results to evaluate force constants in a lattice-dynamical model.

EXPERIMENTAL DETAILS

The stage-2 and -4 samples were prepared by the reaction of the distilled vapors of $SbCl_5$ with a HOPG host material using a two-temperature technique. The details of the sample synthesis have been reported earlier.[1] The samples used in the neutron scattering experiments occupied a volume of $\sim 10\times10\times10$ mm^3, which was constructed by stacking between 10 separate intercalated slabs, each with a *c*-face area of $\sim 10\times10$ mm^2. The widths of the elastic (00*l*) neutron peaks of this stacked configuration were observed to be comparable to the widths observed for a single slab, indicating that no serious misalignment of the *c* axes had occurred. Whereas most intercalated graphite samples are characterized for *c*-axis stacking fidelity using x-ray diffraction, this characterizational method only probes the first ~40 μm of the sample. Thus, although several individual slabs of intercalated graphite were initially characterized using x-ray-diffraction techniques, we first carried out (00*l*) neutron-diffraction scans to ensure the entire ~1 cm^3 of the sample was indeed single-staged material. The (00*l*) elastic neutron scans (300 K) for the stage-2 and -4 $SbCl_5$-graphite system are shown in Figs. 1(a) and 1(b). As can be seen in the figure, the data show that the samples in each case were predominantly single-staged material. Actually, upon careful examination of the neutron data, the (005) reflection of the stage-2 sample and the (002) and (004) reflections of the stage-4 sample show anomalous broadening and asymmetry; however, there is some doubt at this time that these observations indicate mixed staging.

The samples of $SbCl_5$-graphite compounds are stable in air[1] and were not encapsulated for the course of the experiments. Due caution was exercised, however, to prevent excessive moisture from condensing on the samples. The (00*l*) elastic peaks were checked periodically throughout the course of the investigation to monitor the sample condition. The *c*-axis repeat distances for the stage-2 and -4 compounds determined from our neutron-diffraction (00*l*) data are 12.82±0.05 and 19.50±0.05 Å, respectively. [A scan of the stage-2 (11*l*) reflections reveals that a doubling of the *c*-axis lattice constant to 25.64 Å is required to fit intensity data.] These results compare favorably with the published values of 12.74±0.02 Å and 19.60±0.02 Å determined using Mo $K\alpha$ x-rays.[1] It should be mentioned, however, that the value for the stage-2 compound is based on the measurement of the scattering angles of only the (0, 0, 4), (0, 0, 8), and (0, 0, 12) Bragg reflections, since the odd reflections and some of the even reflections show a peculiar shift from the exact angles calculated by Bragg's law of the order of 0.5%. Similar observations were made for the stage-4 compound. They are thought to be due to unusual correlations between the intercalate layers and are reminiscent of effects observed in the stacking behavior of some layer compounds alluded to in the classic paper by Hendricks and Teller.[12,13] These results are being investigated further by both neutron and x-ray diffraction and will be reported in a separate publication.[13]

The diffraction geometry was chosen to observe phonons with both displacements and propagation vector along the *c*-axis.[10] The highest branches correspond to a rigid translation of planes of graphite and intercalant against one another. Referring to Fig. 2, three branches were definitely observed in the stage-2 sample, and five branches were observed in the stage-4 sample. There is weak evidence for the existence of modes at ~180 cm^{-1} which may be associated with intercalation-layer displacements, but further experimental work with larger samples will be necessary to substantiate these preliminary observations.

The lattice-dynamical calculations discussed below are based on a lattice with one, rather than two, intercalate

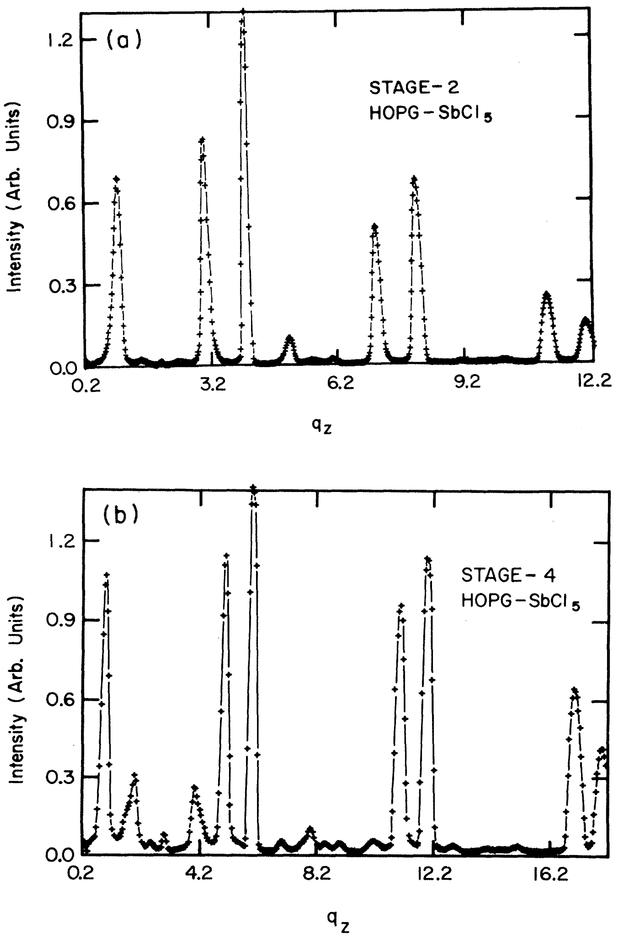

FIG. 1. (00*l*) neutron-diffraction scans of (a) stage-2 and (b) stage -4 graphite-$SbCl_5$ intercalation compounds.

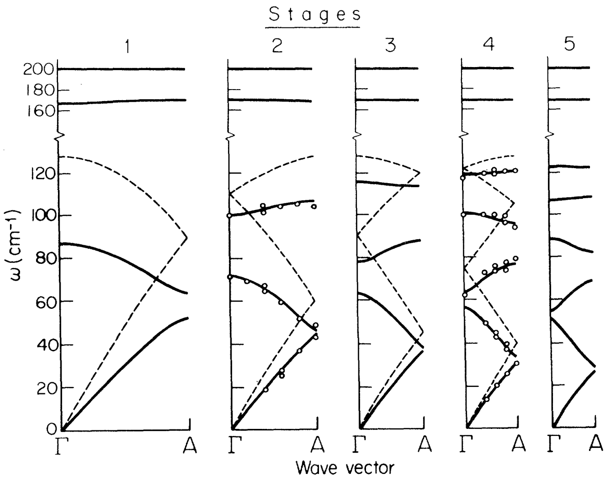

FIG. 2. Longitudinal-phonon modes propagating in the q_z direction in graphite-$SbCl_5$ intercalation compounds. The dashed curve represents the zone folding of the pristine-graphite branch. The open circles for stages 2 and 4 represent our inelastic-neutron-scattering measurements. The solid curves are calculated from the one-dimensional model discussed in the text.

layers per unit cell. However, the observed doubling of the unit cell along the *c* direction would be expected to introduce very small gaps in the dispersion curves and would be difficult to observe experimentally.

ANALYSIS OF THE DATA

A one-dimensional model calculation with nearest-neighbor elastic interactions[9] was carried out, and the stage dependence of the phonon branches was achieved by introducing additional graphite layers into the *c*-axis unit cell and using the same basic set of force constants for all stages (see Table I). The results thus calculated for the low-frequency longitudinal-phonon branches for graphite-$SbCl_5$ compounds of stages 1–5 are shown in Fig. 2 (solid curves), and are compared with the experimental measurements (open circles) and with the zone-folded graphite longitudinal branch (dashed curves).

The hexagonal symmetry of the intercalated graphite requires that the dynamical matrix can be factored into longitudinal and transverse blocks for wave vectors along the Γ—A (q_z direction) in the Brillouin zone. This factorization implies that there is no mixing of the longitudinal and transverse modes along this axis. Consequently, the modeling of the longitudinal *c*-axis modes reduces to a one-dimensional problem with interlayer force constants. This is a rigorous result[14] and has important implications on the more general three-dimensional modeling which is necessary to obtain the higher-frequency branches correctly for all points in the Brillouin zone.[14] In performing the one-dimensional calculations, we have assumed that the Sb-Cl layers move rigidly (infinite intralayer stiffness) and that the interactions between interior graphite layers are identical to those of pristine graphite. The phonon dispersion relations for the highest-stage compounds more nearly approximate the zone-folded pristine-graphite result (dashed curve). The longitudinal modes in Fig. 1 have significantly lower dispersion in the low-stage compounds for the optic branches than in the case for pristine graphite.

DISCUSSION OF THE RESULTS

The force constants listed in Table I indicate that for graphite-$SbCl_5$ compounds the graphite-intercalate coupling is about 20% stronger than the normal interplanar graphite-graphite coupling under the assumption that the intercalate molecule is connected by springs to only six carbon atoms in the graphite bounding layer. The graphite-intercalate is 50% weaker than the graphite-graphite coupling if the intercalate molecule interacts with all 14 carbon atoms in the bounding layer, and if it interacts with ten such carbon atoms, the coupling becomes equal to that in $FeCl_3$. Table I also lists the coupling parameters $\Phi(X\text{-}C_i)$, the force constant between the intercalate and the graphite interior layer adjacent to the bounding layer, and $\Phi(C_b\text{-}C_b)$, which is the force constant between two bounding layers across an intercalate layer. It is noted that in the case of alkali-metal donor compounds, also listed in Table I, the graphite-intercalant coupling is stronger than that in acceptor compounds, a result that is more consistent with the more isotropic electronic properties of alkali-metal intercalation compounds than is observed in typical acceptor compounds. However, intercalation with $SbCl_5$, $FeCl_3$, and K is shown to result in a small decrease in the bonding between the graphite bounding and graphite interior layers.[14] This result suggests that the binding of the graphite to the intercalate layer shifts the π orbitals toward the intercalate and thus weak-

TABLE I. Force constants for the one-dimensional model for longitudinal modes in graphite-$FeCl_3$, graphite-$SbCl_5$, and graphite-Li, K, and Rb. All force constants $\Phi(\alpha\text{-}\beta)$ between layers α and β are normalized to graphite $\Phi(C_i\text{-}C_i)$, and X denotes the intercalant, while C_i and C_b refer, respectively, to the graphite interior and bounding layers. The masses are taken to correspond to the chemical formula $C_{\xi n}X$ and the in-plane density $1/\xi$ is assumed to be constant ($\xi=6.6$ for $FeCl_3$ and 14.1 for $SbCl_5$) independent of stage number n, whereas for lithium $\xi=6.0$ for $n=1$, and for potassium and rubidium $\xi=8.0$ for $n=1$ and 12.0 for $n\geq 2$.

Intercalant	Stage	$\Phi(X\text{-}C_b)$	$\Phi(C_b\text{-}C_i)$	$\Phi(C_i\text{-}C_i)$	$\Phi(X\text{-}C_i)$	$\Phi(C_b\text{-}C_b)$
$SbCl_5$	$n=1$	1.20				−0.067
	$n=2$	1.20	1.0		0.07	−0.067
	$n\geq 3$	1.20	1.0	1.0	0.07	−0.067
$FeCl_3$	$n=1$	0.725				
	$n=2$	0.725	0.879			
	$n\geq 3$	0.725	0.879	1.0		
Lithium	$n=1$	2.900				
Potassium	$n=1$	2.300				
	$n=2$	2.300	0.951			
	$n\geq 3$	2.300	0.951	1.0		
Rubidium	$n=1$	1.870				

ens the bonding to the graphite interior layers.

In addition to inelastic-neutron-diffraction data reported here, ir and Raman spectra on an a-face sample of intercalated graphite could also detect both the intercalate layer modes and the high-frequency modes which are derived from the graphitic A_{2u} and B_{1g} modes at $\sim 870\ \text{cm}^{-1}$,[15] further experimental work in this intermediate range of frequencies is needed. The intercalate layer interactions have relatively little influence on these high-frequency longitudinal modes as compared with the lower-frequency modes shown in Fig. 1.

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

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