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High-pressure neutron-scattering studies of graphite and stage-two graphite-$SbCl_5$

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The longitudinal-acoustic (LA) phonons propagating along the c axis in highly oriented pyrolytic graphite (HOPG) were investigated as a function of pressure up to 20 kbar using inelastic-neutron-scattering techniques. The phonon frequencies varied as $\nu(P,q)=A(P)\sin[c(P)q/2]$, where $A(P)$ and $c(P)$ indicate the pressure dependences of the zone-center LO frequency of B_{1g_1} symmetry and of the c-axis lattice spacing, respectively. From the measurements, the mode Grüneisen parameter for the LA branch was estimated to be 1.5×10^{-2} kbar^{-1} (independent of q); the elastic constant C_{33} for HOPG was found to be 3.40×10^{11} dyn/cm^2 at 1 bar with a pressure coefficient of $(1/C_{33})(dC_{33}/dP)=2.91\times10^{-2}$ kbar^{-1}. The measured c-axis spacings were 6.71 and 12.72 Å for HOPG and stage-2 $SbCl_5$-intercalated graphite, respectively, at atmospheric pressure; the corresponding compressibilities $(1/c)(dc/dP)$ were -2.24×10^{-3} kbar^{-1} (HOPG) and -2.28×10^{-3} kbar^{-1} ($SbCl_5$). Elastic-neutron-scattering studies up to 20 kbar were undertaken to search for stage transformations, but no evidence of any phase transition was observed.

Graphite is a prototype layered solid with the hexagonal crystal structure and space group D_{6h}^4.[1] Graphite intercalation compounds (GIC's) are formed by the chemical insertion of substances of atomic or molecular form between the hexagonal carbon planes.[2–4]

Since neutron scattering requires relatively large sample volumes, it has been used only on compounds based upon pyrolytic graphite host material.[5,6] Such studies are primarily restricted to the c-axis modes because of the almost random orientation of the a axes.[7,8] Zabel *et al.*[9] and Fischer *et al.*[10] have studied a number of metal-donor-GIC's. Quasielastic scattering has been used to investigate phase transitions and melting in HNO_3-graphite.[11] The low-frequency lattice modes in $FeCl_3$ (Ref. 12), Br (Ref. 13), and $SbCl_5$ (Ref. 14) acceptor-intercalated graphite compounds have been measured at room temperature and atmospheric pressure using inelastic-neutron-scattering techniques.

Pressure has been found to cause dramatic changes in the physical properties of GIC's (Refs. 15 and 16) and $SbCl_5$ GIC's have been the subject of many investigations as the material is one of the most air stable.[17–19] Our motivation for choosing this particular compound (besides its stability) was the earlier observation of anomalous electronic behavior induced under pressure.[19]

We have made inelastic neutron-scattering measurements of the longitudinal-acoustic (LA) phonons propagating along the c axis in highly oriented pyrolytic graphite (HOPG) as a function of pressure up to 20 kbar. Values of the mode Grüneisen parameter, the C_{33} elastic constant, and its pressure dependence were calculated from the dispersion curves. Neutron diffraction measurements were also performed on highly oriented pyrolytic graphite (HOPG) to study the variation of the c-axis lattice spacing with pressure.

We were unable to detect any phonons in $SbCl_5$ GIC's under pressure because of excessive scattering by the thick walls of the high-pressure cell. This prevented us from pursuing our original goal of measuring the LA phonon branches in this material as a function of pressure to compare with HOPG. Consequently we were restricted to elastic scattering investigations in the intercalated material. Various Bragg reflections were monitored as a function of pressure to measure the pressure dependence of the c lattice parameter to observe a possible phase transformation.

The highly oriented pyrolytic graphite (HOPG) host material was provided by the Union Carbide Company. The stage-two intercalated graphite-$SbCl_5$ samples were prepared by direct immersion of HOPG specimens in liquid (99.998% purity) $SbCl_5$ at 200 °C for a period of 10 days. The stage index of the samples prepared was characterized by x-ray and neutron diffraction techniques as well as by Raman spectroscopy. HOPG and $SbCl_5$-graphite samples utilized in our neutron-scattering experiments were restricted in size to $\sim4\times4\times5$ mm^3 due to the volume of the capsule in which the samples were confined for the pressure measurements.

The investigations were undertaken using the triple-axis HB-3 spectrometer located at the high flux isotope reactor at the Oak Ridge National Laboratory. Be-[002] and PG-[002] were used as a monochromator and an analyzer, respectively. The incident energy was varied continuously with the final energy (E_f) fixed at 14.796 meV. The sample was oriented with its c axis in the scattering plane. The high-pressure cell[20] used in our experiments is basically a modified version of the one developed by McWhan *et al.*[21] and could sustain pressures as high as 30 kbar at room temperature.

The sample together with a small crystal of KCl with its [001] axis vertical were stacked into an aluminum capsule. A pressure-transmitting fluid (Fluorinert) was added and the capsule was loaded into the high-pressure cell. Pressure was generated using a 100-ton hydraulic press and maintained using a retaining nut. The cell under pressure was installed on the spectrometer and the generated pressure was calibrated against the known pressure dependence of the cubic lattice parameter of KCl. The variation of the KCl lattice constant with pressure was determined independently[20] with the same high-pressure cell.

Pressure studies of the LA phonons at different q values along the [001] axis were carried out between 0 and 20 kbar using constant-Q scans. The measured phonon frequencies were plotted against the reduced wave vector q^* [where $q^*=(c/2\pi)q$] as shown in Fig. 1. Each of the LA branches measured at different pressures was fitted to a simple sine function of the form $\nu(q^*)=A\sin[(\pi/2)q^*]$ and they are represented by the solid lines in Fig. 1. The "A" parameter represents the zone-center longitudinal-optical (LO) out-of-plane phonon of B_{1g_1} symmetry. The frequency of this B_{1g_1} mode (at atmospheric pressure) is 3.808 THz which is in excellent agreement with the value (3.838 THz) reported by Nicklow *et al.*[7] It increases linearly under pressure, with $\partial\nu/\partial P=5.8\times10^{-2}$ THz/kbar. The mode Grüneisen parameter for this mode $\gamma(LO)=(1/\nu)(d\nu/dP)=1.5\times10^{-2}$ kbar^{-1}, which is independent of q for the complete LA branch.

From the initial slope $\Delta\nu/\Delta q$ of the solid lines fitted to the acoustic branches we deduced the corresponding sound velocity, v and the elastic constant, C_{33} via the relation $v^2\rho=C_{33}$ where ρ is the mass density of the material.[15] In the limit of the rigid-layer model, the parameters obtained for $C_{33}(0)$, dC_{33}/dP, and $\gamma_c=(1/C_{33})(dC_{33}/dP)$ are given in Table I. The measured values of the elastic constant C_{33} are in good agreement with previously published data.[7,22–26]

Neutron elastic (00l) scans (for $l=1$, 2, 3, and 4) of HOPG were used to obtain the pressure dependence of the c-axis lattice constant. A least-squares fit to the data gave $c_0=6.70$ Å (the repeat distance of HOPG at atmospheric pressure) and $dc/dP=-1.5\times10^{-4}$ Å/kbar. The c-axis interlayer compressibility, $K_c=(1/c)(dc/dP)=-2.24\times10^{-3}$ kbar^{-1}; it can be compared with -2.10×10^{-3} kbar^{-1} obtained by Lynch and Drickhamer[27] from x-ray studies.

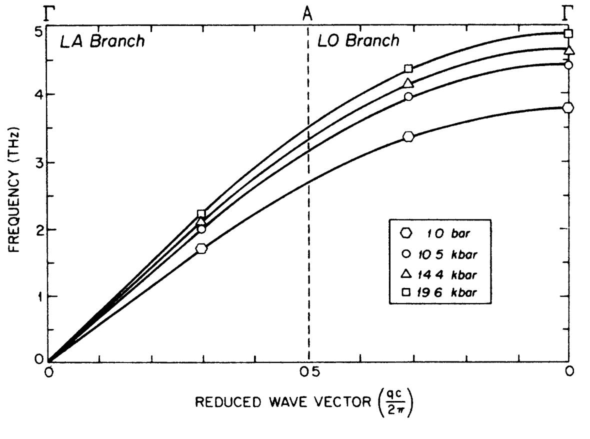

FIG. 1. The phonon energies of the longitudinal-acoustic (LA) branch of HOPG measured as a function of pressure. The solid curve is a fit to the data points using $\nu(P,q)=A(P)\sin[c(P)q/2]$.

The positions of the (00l) Bragg reflection peaks ($l=1,2,3,\ldots,8$) of the SbCl$_5$-graphite sample were investigated at atmospheric pressure. The measured diffractogram illustrated the features of a well-defined pure stage-2 compound with no unreacted graphite peaks. Our initial objective was to perform complementary studies on the graphite-SbCl$_5$ sample similar to the measurements taken on HOPG. Phonons belonging to the LA branch of GIC-SbCl$_5$ were detected at atmospheric pressure outside the pressure cell. However, when the sample was mounted inside the pressure vessel, the corresponding LA phonon intensities decreased considerably. Raising the pressure caused further reduction, and they became virtually impossible to detect with reasonable counting times. Consequently, the inelastic scattering experiments were abandoned due to the limited experimental beam time available. The intensity of the Bragg reflections shows similar reductions and the widths rapidly increased. The (00l) Bragg reflections ($l=1,2,\ldots,8$) were carefully monitored at different pressures (9.8, 14.2, 17.7, and 20.5±0.05 kbar) for any possible stage transformation. Up to 20 kbar there was no indication from the 2θ scans that any type of transition takes place. No new Bragg peaks were observed; those that already existed showed only a broadening and reduction in intensity. The data were fitted to a straight line from which we obtained the parameters given in Table I; they can be compared directly with the complementary results for HOPG. The diffractograms obtained before compression and after decompression indicated that the positions of the Bragg peak reflections were almost identical, but the broadening of the full widths at half maximum was irreversible.

The rapid decrease in the intensities of the Bragg peaks and the irreversible increase in their full widths at half maximum (FWHM's) is attributed to pressure-induced physical damage to the sample. A similar decrease in the Bragg peak intensity and increase in the FWHM's with

TABLE I. Summary of parameters obtained.

	Graphite	Graphite-SbCl$_5$ (stage-2)
c_0 (Å)	6.71	12.72
$\frac{dc}{dP}$ (Å/kbar)	-1.5×10^{-4}	-2.9×10^{-4}
K_c (kbar^{-1})	-2.24×10^{-3}	-2.28×10^{-3}
C_{33} (0) (dyn/cm^2)	$3.4\pm0.02\times10^{11}$	
$\frac{dC_{33}}{dP}$ (dyn/cm^2 kbar)	9.9×10^{9}	
γ_c (kbar^{-1})	2.91×10^{-2}	
α (dyn/cm)	0.0581×10^{5}	
$\frac{d\alpha}{dP}$ (dyn/cm kbar)	0.0185×10^{5}	

pressure was reported by Kim *et al.*[28] in $KHgC_4$. We observed an increase of about 2° in the mosaic spread over the pressure range between 0 and 20 kbar for graphite-$SbCl_5$. Examination of the sample surfaces showed them to be visually distorted with major corrugations, whirls, and grooves of the order of 100 μm. The surface disruption could be due to the pressurizing medium.

A standard derivation of the normal modes (including only nearest-neighbor interactions and a harmonic potential) leads to the relation

$$\nu(q)=\frac{1}{\pi}\left[\frac{\alpha}{m}\right]^{1/2}\sin\left[\frac{\pi}{2}q^*\right] ,$$

$$q^*=\frac{qc}{2\pi}\ ,\text{and } 0\le q^*\le 1 ,$$

where q is the wave vector and ν is the frequency.[29] Since the measured LA branch for graphite (HOPG) has the same dispersion as the one-dimensional chain model $\{\nu(q)=A\sin[(\pi/2)q^*];\ A=1/\pi(\alpha/m)^{1/2}\}$, it is apparent that only nearest-neighbor interactions between graphite layers are relevant for these vibrations.

Our experimental results of the LA dispersion curve fitted to this sinusoidal function gave a C_{33} value of $(3.40\pm0.02)\times10^{11}$ dyn/cm^2 for HOPG. The results agree well with the model calculations of Maeda *et al.*,[30] where interactions up to second-nearest neighbor in plane and first neighbor out of plane were considered. They reported a sinusoidal LA branch and a C_{33} value of 3.65×10^{11} dyn/cm^2. More sophisticated calculations by Al-Jishi and Dresselhaus[31] which include both interplane and intraplane interactions up to fourth-nearest neighbor produce a similar sinusoidal behavior of the LA branch and a $C_{33}=3.69\times10^{11}$ dyn/cm^2. The small variation in the C_{33} values obtained from the different model calculations implies that the interplanar forces are almost entirely restricted to nearest-neighbor planes.

A similar interpretation can be applied at pressures higher than atmospheric (10.5, 14.4, and 19.6 kbar), since the LA branches could be fitted to the same sinusoidal function, $A\sin[(\pi/2)q^*]$, with different A parameters, as illustrated in Fig. 1. Using the relation $\nu(q)=(1/\pi)(\alpha/m)^{1/2}\sin[(\pi/2)q^*]$ and the fact that $\nu(B_{1g_1})=3.808$ THz$=(1/\pi)(\alpha/m)^{1/2}$, the interlayer C—C force constant α was calculated to be 0.0581×10^5 dyn/cm (the mass of the carbon atom, m, was considered as 2×10^{-23} g).

The force constant α varies linearly with pressure; $\partial\alpha/\partial P=0.0185\times10^5$ dyn/cm kbar). For $\nu(q)=(1/\pi)(\alpha/m)^{1/2}\sin[(\pi/2)q^*]$ and $C_{33}=\rho v^2$, then $\gamma_v=(1/v)(dv/dP)=\frac{1}{2}(1/\alpha)(d\alpha/dP)$ and $\gamma_c=(1/C_{33})(dC_{33}/dP)=2(1/v)(dv/dP)=(1/\alpha)(d\alpha/dP)$. These relations show that both $\nu(q)$ and C_{33} should vary linearly under pressure (since $d\alpha/dP$ is constant). This result is consistent with our observations as discussed earlier. The relevant parameters are summarized in Table I.

Inelastic neutron scattering measurements of the longitudinal-acoustic (LA) phonons propagating along the c axis in HOPG showed simple sinusoidal behavior $\nu(q)=A\sin[(\pi/2)q^*]=A\sin(qc/\pi)$, where c is the c-axis lattice spacing. The mode Grüneisen parameter γ was found to be independent of q (since all the phonons propagate along the well defined c axis). The elastic constant C_{33} had a pressure dependence of 2.91×10^{-2} kbar^{-1}. The measured c-axis lattice spacings at atmospheric pressure for HOPG and stage-2 graphite-$SbCl_5$, and the corresponding c-axis compressibilities are given in Table I.

The small difference in the c-axis compressibilities between graphite (-2.24×10^{-3} kbar^{-1}) and stage-2 graphite-$SbCl_5$ (-2.28×10^{-3} kbar^{-1}) indicates that the nature of the c-axis interlayer bonding is predominantly ionic. It also implies that the C—C and the C—$SbCl_5$ nearest-neighbor force constants between two adjacent layers must be quite similar, unlike that reported in many donor-intercalated graphite compounds.[10]

The physical damage that took place within the intercalated sample when subjected to a high-pressure environment was reflected in the rapid decrease of the Bragg peak intensities and increase in the (00l) line widths. These factors contributed to the impossibility of performing pressure studies of the LA branch for GIC-$SbCl_5$ complementary to those undertaken in HOPG. Elastic neutron-scattering studies revealed no evidence of any stage transformation up to 20 kbar and confirm the nonexistence of such a transition up to 14 kbar reported by Houser *et al.*[32] in x-ray pressure studies.

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