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Abstract. The pressure dependences of the Raman-active graphite layer shearing modes in highly oriented pyrolytic graphite (HOPG) and $FeCl_3$–HOPG acceptor intercalation compounds for stage indices $n = 1, 2$ and 3 have been measured in diamond anvil cell by use of Spex-1403 Ramalog system. The results of high-pressure Raman spectra show that both the interior and neighbouring modes exhibit a frequency shift upwards with increasing pressure, which has been attributed to an in-plane lattice contraction. In stage-3 $FeCl_3$–HOPG, the pressure-induced staging transition from stage 3 to stage 4 has been found from the change in intensity ratio of the interior to neighbouring modes at 8.39 GPa. This finding confirmed firstly that the pressure-induced staging transitions are not just confined to the alkali-metal graphite donor intercalations but are valid for the acceptor graphite intercalation compounds.

1. Introduction

Graphite has been a strategically important material for many years. More recently, graphite intercalation compounds (GICs) have also become fascinating and potentially important materials. It has long been recognised that high pressure plays a crucial role in the graphite-to-diamond transformation. Studies of the pressure dependence of GICs, however, began only a few years ago and left much to be explored.

In GICs, the intercalate layers are periodically inserted in the van der Waals gaps of graphite layers and are characterised by a stage index n denoting the number of graphite layers sandwiched between two adjacent intercalate layers. The staging phenomenon is the most fundamental feature of GICs. Safran and Hamann [1] proposed an elastic dipole theory for staging; on the basis of this, one might anticipate structural phase transitions to occur in GICs under a high pressure. The first application of a high pressure to GICs was reported by Clark *et al* [2] in their x-ray studies of KC_{24}. These experiments revealed that reversible transformations of the stage sequence could be induced by pressure. Wada and Solin [3] and Wada [4] subsequently extended the original experiments to different alkali-metal GICs and found similar pressure-induced staging transitions. It is worth emphasising here that those staging transitions are revealed in an interesting way by Wada's high-pressure spectroscopic studies of the Raman-active graphite layer shearing mode E_{2g2} which appears at $\nu = 1580$ cm^{-1} in pure graphite at ambient pressure. Because there are two different environments for the graphite layer in GICs for $n \geq 3$,

next to an intercalant layer (neighbouring layer) or bounded by two other graphite layers (interior layers), the E_{2g2} mode appears as a doublet [5]. The upper frequency component $\hat{E}_{2g2}$ is identified with the neighbouring-layer mode and the lower component E_{2g2}^0 with the interior graphitic mode. The relative intensities of the two modes change with the stage index n; as higher stages are approached, the interior mode dominates. The spectra for $n = 1$ and 2 exhibit only a single peak $\hat{E}_{2g2}$, consistent with the absence of interior layers for these stages. In the intercalation reaction process, a transfer of electronic charge takes place. Thus, GICs are classified into donor or acceptor compounds according to whether charge is transferred to or from the graphite host. Alkali-metal graphite intercalation compounds (AGICs) are the best-investigated materials among the donor compounds. To date, some hundreds of different GICs of both donor and acceptor types have been synthesised. However, there seems to be no study of pressure-induced staging transition for the acceptor compounds. Hence the present investigation was undertaken. In view of their stability in air, ferric chloride ($FeCl_3$)–graphite samples may be safely removed from their encapsulating ampoules for short periods of time and therefore provide prototype samples for properties measurements under a high pressure. The present high-pressure Raman studies on well characterised $FeCl_3$–graphite samples, while supporting previous findings on the relative intensity of the doublet components, represent the first systematic study of the pressure-induced staging transition for the acceptor compounds. Because of the strong connection between the E_{2g2}-like modes in GICs and E_{2g2} mode in pure graphite, the high-pressure Raman spectra for pristine graphite are also included for purposes of comparison.

2. Experimental details

Employing highly oriented pyrolytic graphite (HOPG) as a host material, $FeCl_3$–HOPG intercalation compounds, essentially single staged $n = 1$, 2 and 3, were prepared using the conventional two-zone system [6]. A miniature Mao–Bell diamond anvil cell [7] with gasket was used to generate the high pressure for Raman measurements. Methanol–ethanol–water (16:3:1) was used as a pressure-transmitting medium for HOPG measurements. For $FeCl_3$–HOPG, no pressure-transmitting medium was used to prevent possible chemical reaction under a high pressure. The pressure was calibrated by the ruby fluorescence technique [8]. Raman spectra were taken in the back-scattering configuration, using a point-focused 4880 Å Ar-ion laser incident beam and a Spex-1403 Ramalog double monochromator equipped with a Datamate.

3. Results and discussion

Figure 1(a) shows the Raman spectra of the 1580.0 cm^{-1} E_{2g2} mode in the pristine HOPG (approximately $n \to \infty$) taken at several different pressures at room temperature. The high-pressure Raman spectra of the E_{2g2}-like mode in $FeCl_3$–HOPG for $n = 1$, 2 and 3 are given in figures 1(b), 1(c) and 1(d), respectively. Figure 2 shows the results of these Raman frequencies as a function of pressure. The zero-pressure Raman frequency ν_0 and the rates $\partial \nu_0 / \partial p$ of Raman frequency shift with respect to pressure of $FeCl_3$–HOPG ($n = 1$, 2, 3 and ∞) are listed in table 1. The weak band or shoulder seen only in the spectra in figure 1(b), which was caused by the impure sample with $n = 1$, are not
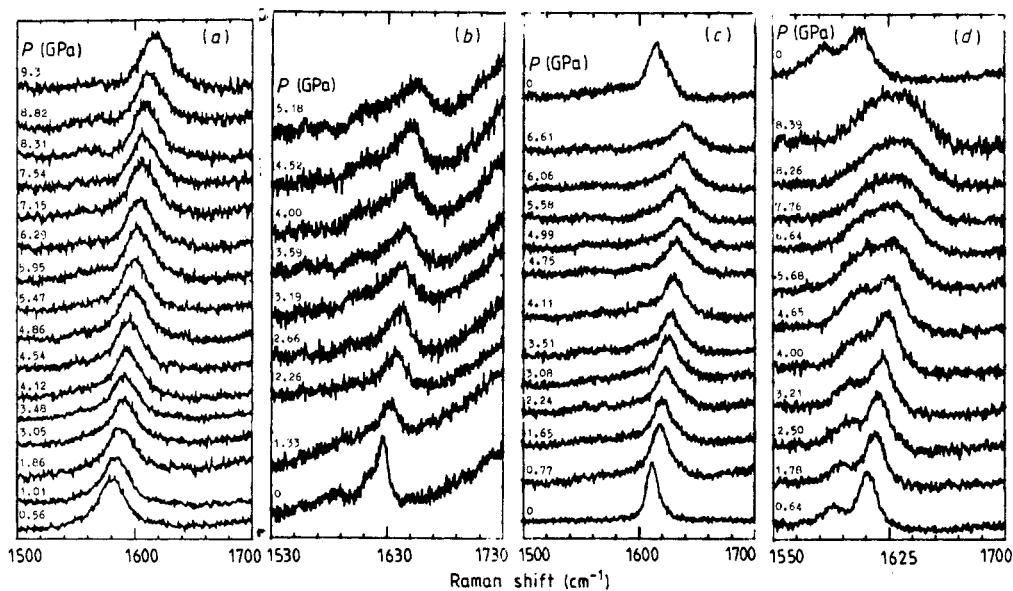
Figure 1. Raman spectra of HOPG and FeCl$_3$–HOPG taken at different pressures and room temperature: (*a*) HOPG (approximately $n \to \infty$); (*b*) FeCl$_3$–HOPG ($n = 1$); (*c*) FeCl$_3$–HOPG ($n = 2$); (*d*) FeCl$_3$–HOPG ($n = 3$).
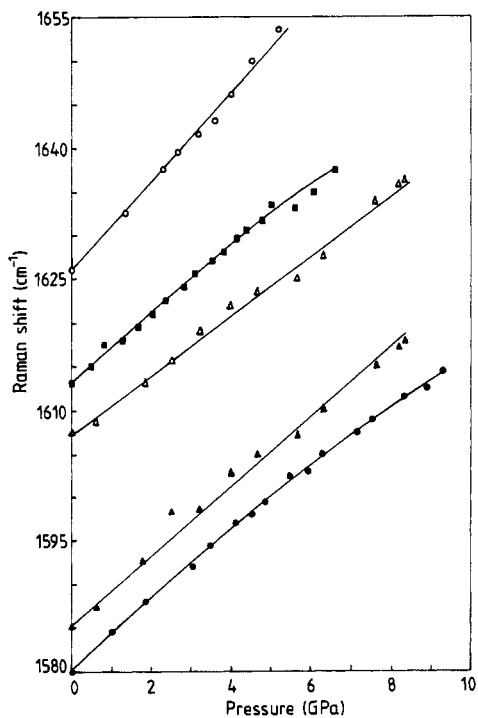

Figure 2. Raman shifts in HOPG (●) and FeCl$_3$–HOPG for $n = 1$ (○), $n = 2$ (■) and $n = 3$ (▲, interior mode; △, neighbouring mode) are plotted as a function of pressure: ——, least-squares best fits of the experimental data points.

Table 1. The zero-pressure Raman frequency ν_0 and the rates $(\partial\nu_0/\partial p)$ of Raman frequency shifts with respect to pressure of $FeCl_3$–HOPG for $n = 1, 2, 3$ and ∞, measured below the highest pressure P_{max}.

Stage n	Mode		ν_0 (cm^{-1})	$\partial\nu_0/\partial p$ (cm^{-1} GPa^{-1})	P_{max} (GPa)
1	Neighbouring,	$\hat{E}_{2g2}$	1626.0	5.3	5.18
2	Neighbouring,	$\hat{E}_{2g2}$	1613.0	3.9	6.61
3	Neighbouring,	$\hat{E}_{2g2}$	1607.5	2.9	8.39
	Interior,	E_{2g2}^0	1585.0	4.1	8.39
∞		E_{2g2}	1580.0	4.1	9.30

included in the plot in figure 2. It is well known that pure samples with $n = 1$ are difficult to prepare.

Comparing the different stages of $FeCl_3$–HOPG listed in table 1, several trends are apparent. Firstly, both the interior and the neighbouring modes exhibit a frequency shift upwards as a function of the reciprocal of the $1/n$ stage. This lattice mode hardening has been attributed to an in-plane lattice contraction associated with acceptor intercalation [9]. Secondly, both the interior and the neighbouring modes shift upwards with increasing pressure. The pressure results in an in-plane lattice contraction and hence a lattice stiffening or a shift in mode frequency upwards, similar to the acceptor intercalation-induced lattice contraction. The effect of pressure on the Raman spectra for $n = 1$ tends to be anomalous; its rate of mode frequency shift upwards is considerably greater than that of pristine HOPG, resulting from the environment of each graphite layer for $n = 1$, much unlike the situation for $n \geq 2$. As regards the different shift in rates upwards for interior and neighbouring modes ($n = 3$), it could be interpreted in terms of a different strain within both the interior and the neighbouring graphite layers under pressure, a condition also necessary to induce a staging transition from $n = 3$ to 4. The pressure-induced staging transition has been determined from figure 1(d).

In order to clarify this transition explicitly, we have carried out the component Lorentzian shape analysis of the spectra shown in figure 1(d) with the following conditions.

(i) In view of the fact that the interior and neighbouring modes can be well distinguished under lower pressures, the bands which become broadened under higher pressures still consist of the same modes.

(ii) The non-hydrostatic pressure effects that both interior and neighbouring modes suffered are equivalent; therefore the full widths at half-maximum for the two modes are essentially equal.

The analytic results of the spectra at several pressures are shown in figure 3 and listed in table 2. As we predicted, the relative ratio of integrated intensity of the interior mode (1585 cm^{-1}) to that of the neighbouring mode (1607.5 cm^{-1}) increases with increasing pressure. As a result the number of interior layers increases, whereas the number of neighbouring layers decreases during the staging transition. For stage $n = 4$, where the number of interior and neighbouring layers are equal, the two modes have approximately equal intensities. According to this, the staging transition pressure was determined to
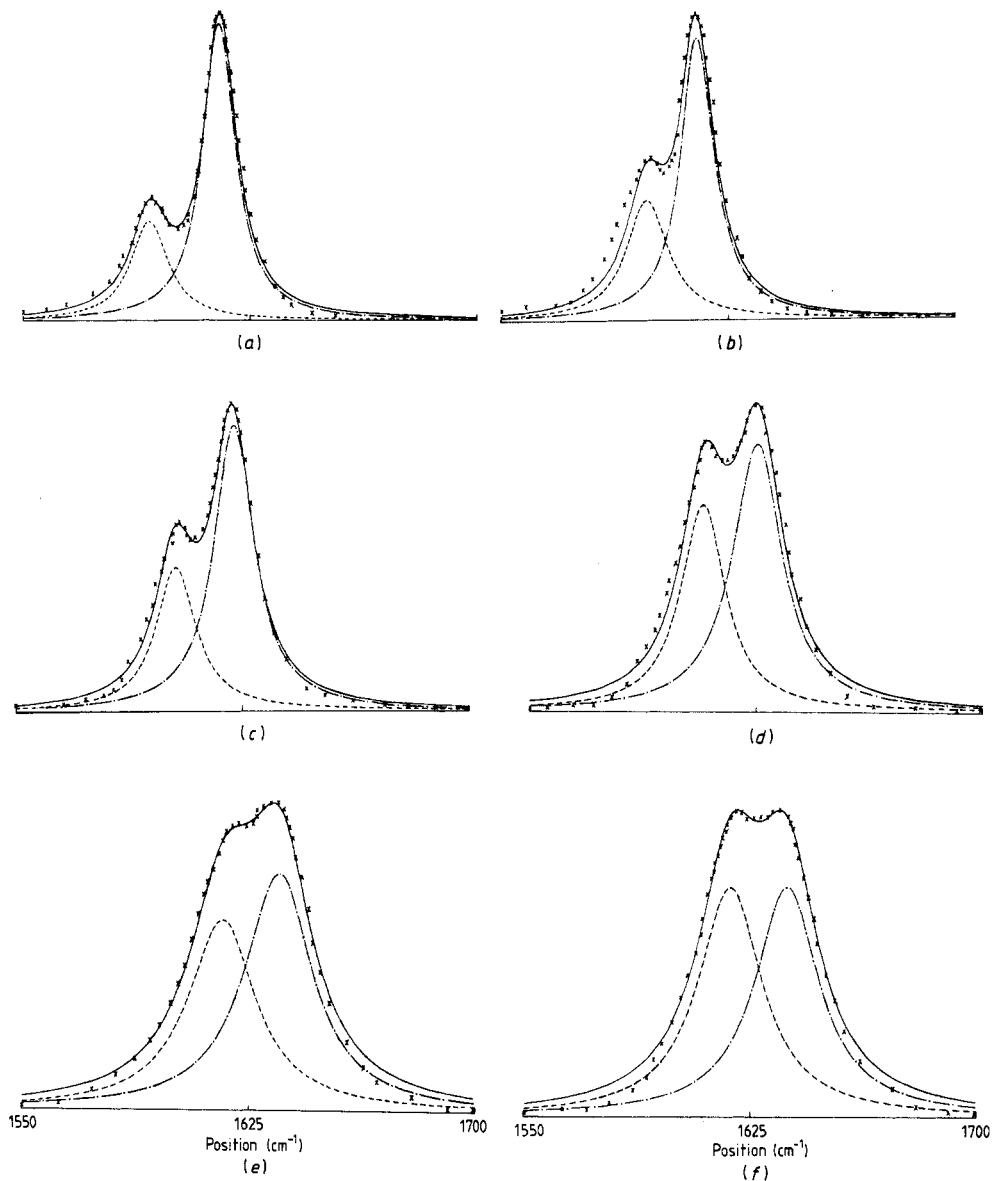
Figure 3. The component Lorentzian shape analysis of the Raman spectral data ($\times$) taken from figure 1(d) at several pressures: (a) 0.64 GPa; (b) 2.50 GPa; (c) 4.00 GPa; (d) 5.68 GPa; (e) 7.76 GPa; (f) 8.39 GPa.

be 8.39 GPa. The Raman spectrum R in figure 1(d), which was taken after releasing the pressure, shows similar features to the spectrum taken at 0.64 GPa in figure 1(a). This proves that the staging transition is reversible. Finally, it must be pointed out that this staging transition needs to be confirmed by further detailed high-pressure x-ray experiments.

Table 2. The positions and relative integrated intensities of interior and neighbouring modes at several pressures.

Pressure (GPa)	Position (cm^{-1})		Relative intensity (%)	
	Interior	Neighbouring	Interior	Neighbouring
0.64	1587.2	1608.5	27	73
2.50	1598.5	1615.5	34	66
4.00	1603.0	1622.0	33	67
5.68	1607.0	1625.0	41	59
7.76	1615.5	1634.0	44	56
8.26	1617.0	1636.0	48	52
8.39	1618.0	1637.0	50	50

We conclude that staging transitions under high pressure are not just confined to AGICs. In fact, the systematic studies on FeCl$_3$–HOPG for stage $n = 3$ show that a staging transition similar to that in AGICs also occurs in this acceptor compound at a much higher pressure. No staging instability, however, was observed in stage 1 and 2 up to 5.18 GPa and 6.61 GPa, respectively.

Acknowledgment

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