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2 Synthesis and characterisation of a new graphitic C-S compound
3 obtained by high pressure decomposition of CS₂

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5
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11
12 **Abstract**

13 Carbon disulphide (CS₂) is, together with its closest analogue CO₂, one of the simplest
14 molecular systems made of double covalent bonds. Under high pressure, the molecular
15 structure is expected to break up to form extended crystalline or polymeric solids. Here we
16 show that by compression at 300 K to ~10 GPa (100 kbar) using large-volume high pressure
17 techniques, a sudden reaction leads to a mixture of pure sulphur and a well-defined
18 compound with stoichiometry close to C₂S which can be recovered to ambient pressure. We
19 present neutron and x-ray diffraction as well as Raman data which show that this material

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20 consists of sulphur bonded to sp^2 graphite layers of nanometric dimensions. The compound is
21 a semiconductor with a gap of 45 meV, as revealed by temperature dependent resistivity
22 measurements, and annealing at temperatures above 200 °C allows to reduce its sulphur
23 content up to $C_{10}S$. Its structural and electronic properties are fundamentally different to
24 “Bridgman black” reported from previous high pressure experiments on CS_2 .

25

26 Keywords: graphite, high pressure, carbon disulphide, neutron scattering, Raman scattering.

27

28 **1. Introduction**

29 The general trend in molecular systems under compression is that they solidify (in most cases
30 crystallise) in the GPa range and at sufficient high pressure ultimately form extended
31 crystalline or amorphous compounds as the molecules break up [1]. These high pressure solids
32 have vastly different electronic properties compared to the starting material and in some
33 cases can be quenched to ambient pressure where they may have useful properties. A well-
34 known example is carbon-monoxide (CO) which transform under pressure of 5 GPa to a
35 polymeric compound which can be recovered to atmospheric pressure and which is a high-
36 density energy material [2]. Another case is CS_2 , a colourless liquid with a strong odour which
37 is isostructural to CO_2 . Following a reaction route indicated by Bridgman [3], CS_2 transforms
38 at 3-5 GPa and ~ 250 °C into a black solid (« Bridgman black ») which can be recovered to
39 ambient pressure and temperature. Analysis suggests that it consists of a disordered 3D
40 network with the same stoichiometry as CS_2 and highly crosslinked chains with both single and
41 double C-S bonds [4-11]. The material is a semiconductor [6] with a poor electrical conductivity
42 of $10^{-13} \text{ Ohm}^{-1}\text{cm}^{-1}$. Compression at 300 K (without heating) in a diamond anvil cell leads to a

43 transition at 8-10 GPa which is governed by kinetics [9], and it appears that the structure of
44 the polymer depends on the specific experimental conditions it has formed [10].

45 Here we report the transformation of CS₂ in the 10 GPa range, at ambient temperature, using
46 a large-volume (“Paris-Edinburgh”) pressure device. This technique allows to load and
47 compress ~100 mm³ liquid samples, i.e. macroscopic quantities, between two opposed anvils
48 and a metallic gaskets. It can be used for both in-situ characterisation by neutron and x-ray
49 diffraction as well as ex-situ sample synthesis, see ref. [12] for a detailed description of the
50 method. Our investigations involved two types of experiments: In a first measurement, the
51 transformation of CS₂ was observed and studied by in-situ neutron diffraction to 9 GPa. These
52 revealed a sudden transition at ~ 8 GPa from a crystalline molecular solid to a disordered
53 compound which can be recovered to ambient pressure. In a second type of experiments, the
54 recoverability of the sample was exploited to produce in several loadings a considerable
55 amount of material (~0.5 cm³) at atmospheric pressure. The availability of such macroscopic
56 sample quantities at ambient pressure, outside the pressure cell, then enabled us an in-depth
57 characterisation of the reaction product by applying a variety of techniques, in particular x-ray
58 and additional neutron diffraction, Raman scattering, infrared absorption, density and
59 resistivity measurements.

60 **2. Experimental**

61 **2.1 Neutron diffraction at ambient and high pressure**

62 In-situ high pressure diffraction measurements were carried out at the PLANET beamline of
63 the Japanese neutron Facility MLF at J-PARC, Tokai, Ibaraki [13] using a VX4 Paris-Edinburgh
64 press [12]. Approximately 30 mm³ of CS₂ purchased from Wako Pure Chemical Industries Co.
65 Ltd (Japan) was loaded into double-toroidal sintered diamond anvils and null-scattering TiZr

66 gaskets. The sample was then compressed at 300 K in steps of 1-2 GPa, up to ~8 GPa where it
67 transformed suddenly. Pressures were determined to a precision of ± 1 GPa by the load on
68 the anvils and a pre-determined calibration curve. Data in the crystalline phase (below 8 GPa)
69 were analysed by Rietveld refinement using FullProf [14]. Once the transformation occurred,
70 the sample was decompressed in steps to 0 GPa, again with data taken during the download.
71 Neutron diffraction patterns at ambient pressure from recovered and purified samples (see
72 sections 2.2 and 2.3) were collected in a vanadium can. Pair correlation functions $g(r)$ of the
73 patterns $S(Q)$ were obtained with the software package *0529_FourierTranslation.exe*
74 developed by Kyushu University/Dr. Kohara (SPring8) (Japan) using number densities of ρ_0
75 $=0.01419/\text{\AA}^3$ and $\rho_0 =0.0104/\text{\AA}^3$ for the un-annealed and annealed samples, respectively.

76 **2.2 Ex-situ (off-line) sample production**

77 Since the *in-situ* neutron data demonstrated that the sample obtained at high pressure can be
78 recovered to ambient pressure, a series of samples were produced in off-line runs using single-
79 toroidal tungsten carbide anvils [12] and copper beryllium gaskets, with a VX3 Paris-Edinburgh
80 load-frame. This different anvil/gasket configuration allowed a much larger sample volume of
81 initially 106 mm^3 , as well an easy extraction of the sample pellet from the metallic gasket.
82 Again, the transition occurred suddenly and was observable by and audible “click” and a drop
83 in load at 72 ± 3 tonnes on the anvils, which corresponds to 7-8 GPa according to a calibration
84 curve for such anvils. The transition is perfectly reproducible and was observed in at least 20
85 runs, half of them in runs concerned by this report. Samples were decompressed to ambient
86 pressure at a speed of ~ 1 GPa/min. Liquid CS_2 was purchased from ARCOS ORGANICS (99.9%)
87 and Tokyo Chemical Industry (98%) and loaded into the cell using a previously described

88 method [15]. The source of the samples had no observable influence on the outcome of the
89 experiments.

90

91 **2.3 Sample purification, determination of density and stoichiometry.**

92 Visible observation of the sample after extraction from the pressure cell revealed an
93 inhomogeneous compound of crystalline sulphur in a matrix of black material (see Results
94 section). To remove the sulphur, the pellet was filed, then thoroughly grinded in liquid CS₂ and
95 stirred in a high-power ultrasonic bath to dissolve the sulphur. The turbid fluid was centrifuged
96 at 7500 rpm to sediment the black micrometer-size particles, and the whole procedure was
97 repeated a second time with fresh CS₂. After drying in vacuum, the powder appeared
98 homogeneous and no trace of crystalline sulphur could be detected neither visually nor by
99 Raman scattering.

100 The average density of the inhomogeneous pellet was then measured by Archimedes' method
101 using distilled water and an electronic balance model L432 from BEL Engineering (resolution:
102 1 mg) and its associated DENS-01 density kit. Given the initial mass and volume of the pellet,
103 the mass of the powder after removal of sulphur as well as the known density of crystalline
104 sulphur, the density and stoichiometry x and of the remaining homogenous material C _{x} S could
105 be easily determined to an accuracy of 2% and 5%, respectively.

106 **2.4 Raman and infrared measurements**

107 Raman experiments were carried out using a confocal in-house optical set-up using a Jobin-
108 Yvon/Horiba HR-460 spectrometer equipped with a monochromator with 1500 grooves/mm
109 and a Peltier-cooled Andor CCD. Raman scattering was excited by a continuous argon ion laser

110 emitting at 514.5 nm and focused onto a spot of about 2 μm . Spectra were collected in
111 backscattering geometry with maximal 7 mW laser power on the powder sample. Infrared
112 measurements were performed on a Bruker IFS66V/S Fourier transform infrared
113 spectrometer working in vacuum and aligned in transmission geometry. Spectra were
114 acquired in the frequency region 600-8000 cm^{-1} with resolution of 4 cm^{-1} and accumulation of
115 10 scans using the mid infrared instrumental configuration with Globar, KBr and MCT as
116 respectively source, beam splitter and detector. A homogeneous pellet of 13 mm diameter
117 was prepared by mixing 1 mg powder sample with 200 mg grinded and dried KBr powder as
118 transparent matrix material.

119 **2.5 X-ray diffraction and gravimetric measurements**

120 X-ray diffraction data of the purified samples were obtained on an Xcalibur-S 4-circle
121 diffractometer from Rigaku (Agilent) with a Sapphire CCD detector and a Mo anode (17.4 keV),
122 and the samples filled into a 1 mm kapton capillary. Diffraction patterns from the sample and
123 the empty capillary were collected up to $Q=15 \text{ \AA}^{-1}$ in transmission geometry and the azimuthal
124 integration of the 2D patterns was done with the CrysAlisPro software (CrysAlisPro
125 1.171.38.46, Rigaku Oxford Diffraction, 2015). After subtraction of the capillary contribution,
126 the pair distribution function was obtained from the Fourier transform of the scattering
127 function $S(Q)$ using the PDFgetx3 program [16]. Thermogravimetric measurements used a
128 Q600 SDT from TA Instruments with Pt crucibles under nitrogen flow. The sample with initially
129 a mass of approximately 10 mg was heated at a rate of 3 K/min from 20 $^{\circ}\text{C}$ to 700 $^{\circ}\text{C}$.

130 **2.6 Transmission and Scanning Electron Microscopy (TEM/SEM)**

131 Transmission Electron Microscopy (TEM) measurements were carried out using a JEOL 2100F
132 field emission gun instrument operating at 200 kV in combination with an UltraScan 4000

133 Gatan CCD camera and an energy dispersive x-ray detector with 140 eV resolution for
134 elemental mapping. For Scanning Electron Microscopy (SEM) measurements we used a Zeiss
135 Ultra 55 field emission gun SEM operated at 15 kV. Backscattered electron or secondary
136 electrons modes were applied to investigate the morphology. Energy dispersive X-ray
137 spectrometry (EDXS) point analysis was carried out at a working distance of 7.5 mm using an
138 EDXS QUANTAX system equipped with a silicon drift detector XFlash 4010 (Bruker). Data were
139 processed with the software Esprit (Bruker).

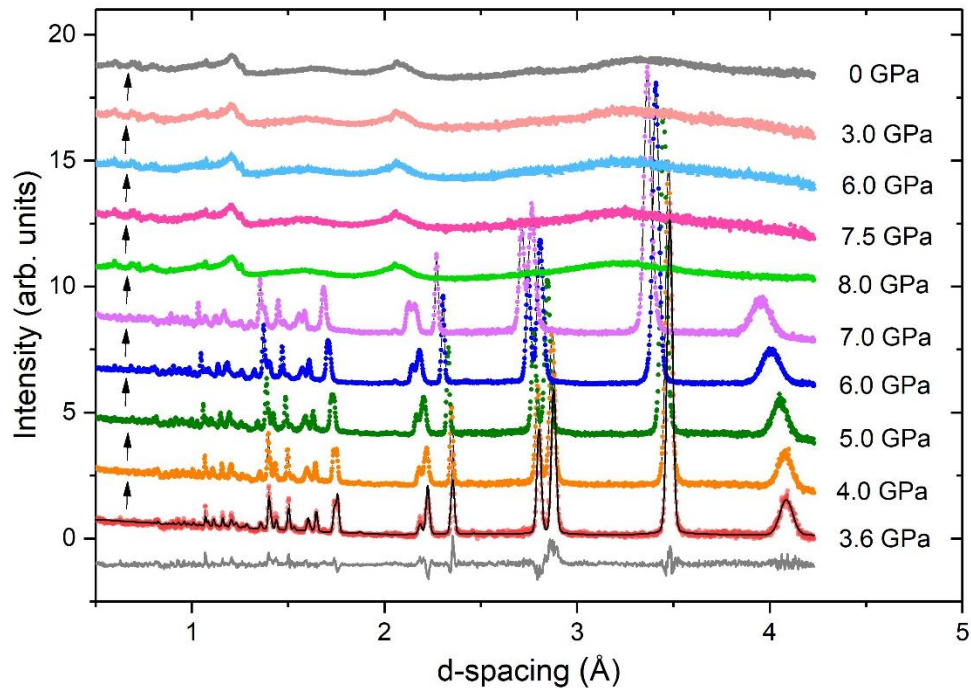
140 **2.7 Electrical resistivity measurements**

141 Four-probe DC resistivity measurements were carried out with a laboratory-made sample
142 holder consisting of two electrically insulated Al-plates which compact the powder sample on
143 a strip of 7 mm length and 0.3x1.0 mm² cross section. The sample holder was then attached
144 and electrically contacted to a standard sample “puck” with its associated sample stick from
145 Quantum Design. The measurements were carried out with a PPMS (Quantum Design)
146 between 2 and 300 K using a current limit of 100 μ A and a cooling/heating rate of 1 K/min.
147 Varying the current showed ohmic behaviour of the resistivity.

148 **3. Results**

149 We first report the *in-situ* observation of the high pressure transformation of CS₂ by neutron
150 diffraction (Fig. 1). The crystalline phase below 8 GPa can be well fitted by the known *Cmca*
151 structure [17] with no detectable contaminant in the diffraction patterns. Rietveld
152 refinements show an anisotropic compression of the structure with no change of the C=S bond
153 length to within ± 0.01 Å (the precision of the technique) nor a change in the orientation of
154 the molecule in the unit cell. At a load of 71 tonnes corresponding to 7.9 GPa, the load
155 suddenly dropped by 1 tonne and the diffraction pattern revealed a transformation to a

156 strongly disordered (amorphous) solid. Diffraction patterns were collected for the following
157 12 hours where no further change could be observed, indicating that the transition was
158 complete.

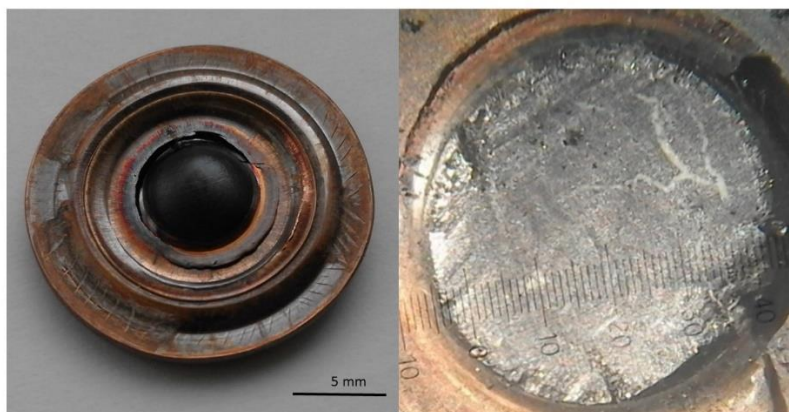


159
160 Fig. 1 Neutron diffraction patterns of CS₂ as a function of pressure. Patterns were shifted
161 vertically for clarity. Arrows indicate sequence of data collection. The line through the data at
162 3.6 GPa is a Rietveld fit and the grey line below the difference curve. Errors in pressure values
163 are estimated to ± 0.5 GPa in the upstroke and ± 1.5 GPa in the downstroke.

164 The sample was then decompressed in 4 steps (60, 40, 20, 5 tonne corresponding to an
165 estimated 7.5, 6, 2 and 0 GPa, respectively) and no changes could be observed apart from a
166 trivial shift of all features to larger *d*-spacings as the load (pressure) is decreased. The sample
167 obtained at high pressure is hence recoverable to ambient pressure, with no apparent
168 modifications except a decrease in density.

169 After these observations, the experiment was repeated with a different gasket-anvil setup
170 allowing three times more volume per loading and an easy extraction of the recovered sample.
171 The aim was to produce larger sample quantities, at ambient pressure, which allow a detailed
172 characterisation by various other methods which cannot be carried out in the pressure cell.
173 Runs using this setup gave reproducibly spherical black spheres of ca. 6 mm diameter inside
174 the metallic gasket with no trace of remaining liquid (Fig. 2). Observation under a laboratory
175 microscope shows an inhomogeneous sample with yellowish streaks within a matrix of black
176 material. Micro-Raman measurements identified the yellow component as crystalline octa-
177 sulphur, as expected, by comparison with the known Raman spectrum. Since we were
178 interested only in the black homogeneous material, the sulphur was removed by dissolving
179 the grinded powder in liquid CS₂, as explained above. It was checked by Raman scattering that
180 this procedure does not modify the remaining component. The density of the initial
181 (inhomogeneous) pellet was determined by Archimedes' method (see above) and gave a value
182 of $1.95 \pm 0.03 \text{ g/cm}^3$. From this and the mass of the powder after removing the crystalline
183 sulphur, a composition of approximately C₂S and a density of $1.76 \pm 0.03 \text{ g/cm}^3$ was determined
184 for the remaining compound. This value might be compared to the density of pure graphite
185 (2.26 g/cm^3) and pure crystalline sulphur (2.07 g/cm^3). For simplicity, we will call this
186 compound "C₂S" in the following.

187

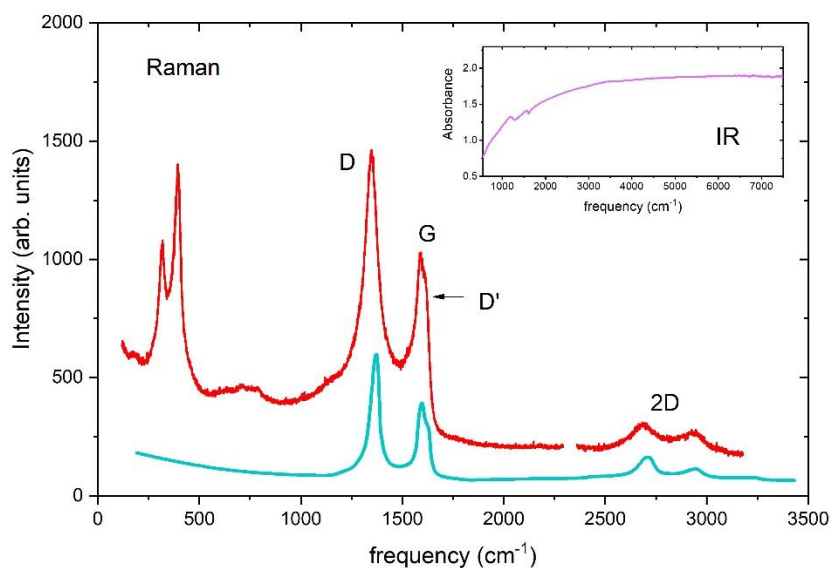


188

189 Fig. 2. Left: Sample (black sphere in the centre) surrounded by the brownish metallic gasket,
190 after extraction from the pressure cell. Right: Close-up view on the sample, after filing the
191 pellet to obtain a flat surface. Note the yellow streaks from crystalline octo-sulphur.

192

193 The Raman spectrum (Fig. 3) of this purified black powder revealed immediately a nano-sized
194 graphitic compound, i.e. a material made of sheets of carbon on a honeycomb lattice. Such
195 material, which includes pyrolytic graphite and graphene, has been extremely well
196 characterized by Raman scattering [18-20]. Its characteristic fingerprints are: The G-peak at
197 1586 cm^{-1} , the D-band at 1350 cm^{-1} , the 2D peak at 2690 cm^{-1} as well as an additional feature
198 at 2940 cm^{-1} which appears in material with large disorder. The ratio of the D and G peak
199 varies with the particle size and can be used to determine the average linear dimension of the
200 carbon sheets [19] which gave $\sim 25\text{ \AA}$ in our case. In addition, the position of the G-band at
201 1585 cm^{-1} indicates a pile-up of only few carbon-layers in each crystal [20].



202

203 Figure 3: Raman spectra (main figure, upper red curve) and infrared absorbance (inset) of C₂S.

204 The lower (blue) Raman spectrum are published data of disordered graphite [18] (called

205 “glassy carbon” in [18]).

206

207 A significant difference compared to pure graphite or its various disordered forms is the

208 existence of two intense peaks at 318 and 394 cm⁻¹ which are absent in any of the latter

209 materials. The peaks cannot be assigned to modes of remaining CS₂, nor to vibrations of

210 residual crystalline sulphur, nor to those of S₈ or even S₂ monomers which have no modes

211 between 250 and 410 cm⁻¹ [21]. Since SEM and TEM measurements (see further below) show

212 the presence of only two elements, carbon and sulphur, these modes have to be ascribed to

213 vibration of C-S bonds formed between the carbon sheet and sulphur atoms. In contrast to

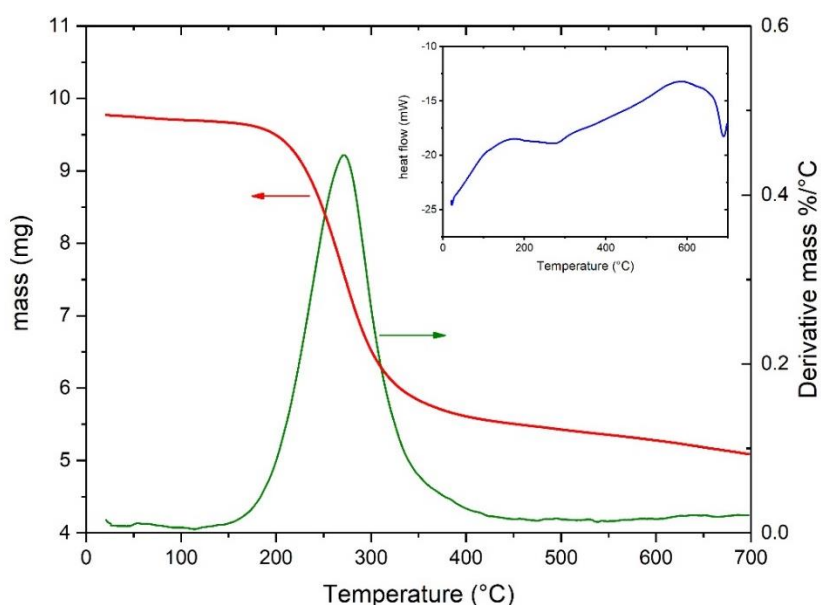
214 the Raman data, the measured infrared absorbance in the 500-7000 cm⁻¹ range (inset fig. 3) is

215 almost featureless showing only two weak, broad and distorted features of at 1200 cm⁻¹ and

216 1575 cm⁻¹. The latter is reminiscent to one of the two IR active modes in graphite (868 cm⁻¹

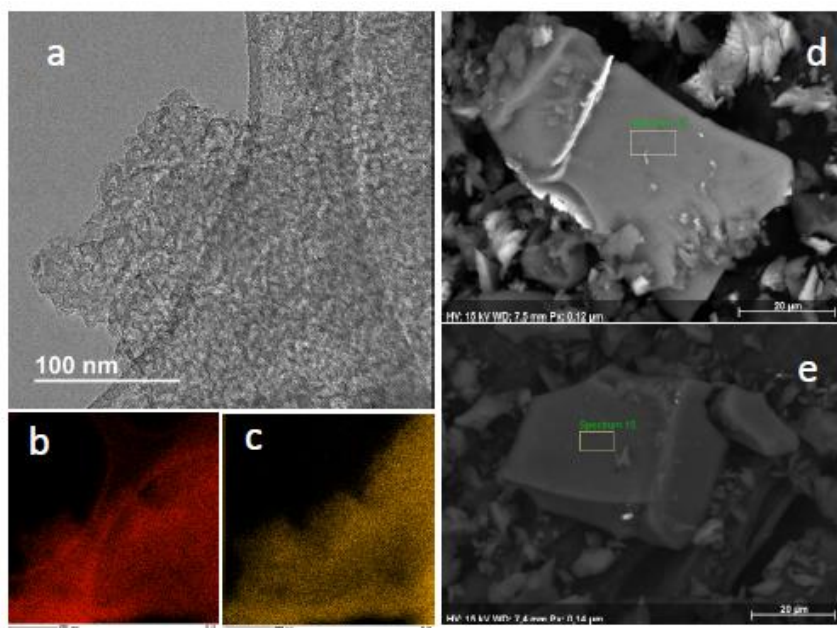
217 and 1588 cm⁻¹) [22]. Note that single-layered graphene has no IR mode at all.

218 To invest the thermal stability of the compound, thermogravimetric measurements were
219 carried out between 20 and 700 °C, see fig. 4. It is found that C₂S starts to decompose at ~200
220 °C reaching the maximum speed of transformation at 260 °C. The transformation is complete
221 at ~350 °C after which the sample has lost approximately 50% of its mass.



222
223 Fig. 4: Thermogravimetric data showing the loss of mass (red line, left scale) and its derivative
224 (green line, right scale). The inset shows the associated heat transfer.

225
226 Since the initial stoichiometry (C₂S) as well as the change in mass is known, the annealed
227 compound must still contain approximately 9 at% of sulphur, i.e. must have a composition of
228 approximately C₁₀S. From the measured net heat flow during the transition we estimate the
229 total amount of energy absorbed by the process to 3.7 J, i.e. 30 kJ per mole of released sulphur.
230 This number is typically in the range of a strong van der Waals or ionic binding, i.e. the released
231 sulphur is certainly not covalently bonded to carbon.



232

233 Figure 5: Representative TEM (a) and SEM (d,e) images of un-annealed (a,d) and annealed (e)
 234 samples. Image (b) and (c) show carbon and sulphur distribution in a similar flake as shown in
 235 (a). The convex structure visible in (a) and (b) is the sample holder, a Lacey carbon grid. The
 236 measured sulphur content is 33 at% in (d) and 14 at% in (e). TEM measurements were carried
 237 out at 80 K to reduce sample damage from electron bombardment.

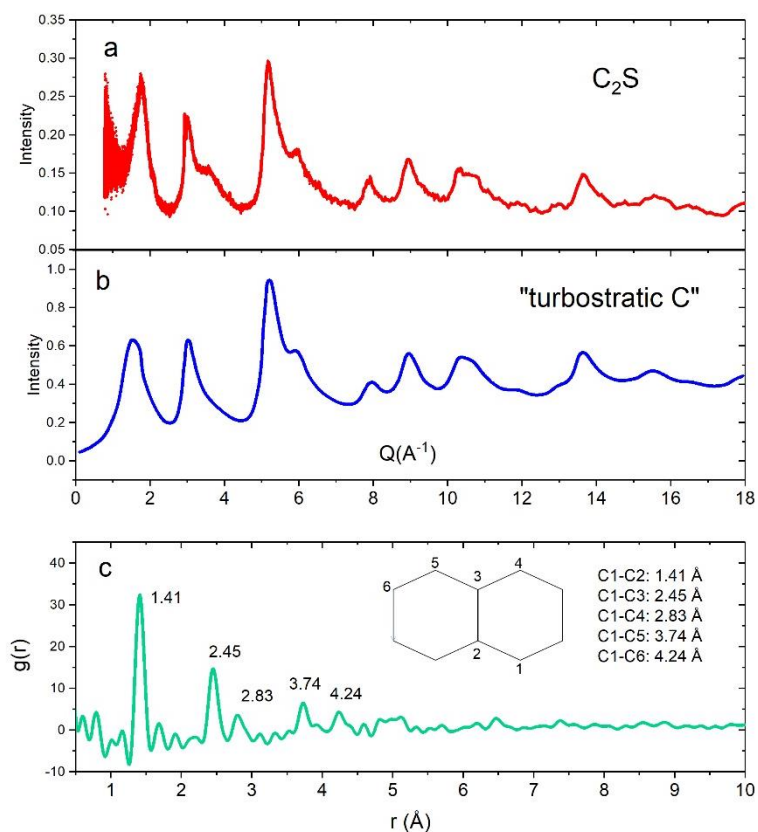
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239 Next, Scanning and Transmission Electron Microscopy (SEM and TEM, respectively) were
 240 carried out which support the average chemical compositions of the samples cited above but
 241 reveal a large spread in stoichiometry: Fig. 5 shows representative SEM and TEM images which
 242 find that the sulphur composition in the un-annealed sample (“C₂S”) varies between typically
 243 10 and 40 at% between different grains. In the annealed samples (“C₁₀S”) it is between
 244 approximately 5 and 20 at%, and this composition remained approximately constant even for
 245 samples heated to 700 °C. Clearly, about 10% of the initial 30 at% sulphur must be tightly
 246 bonded to carbon. It was also found that the un-annealed samples were prone to changes in

247 their visual aspect during electron bombardment. This must hence be related to migration of
248 loosely bonded sulphur, the same fraction which can be removed by heating.

249 The structure of the powder samples was then determined by neutron and x-ray diffraction
250 applying a pdf analysis, as appropriate for disordered systems. We note that given a
251 composition of initially C_2S , the scattering of neutrons is almost completely dominated by
252 carbon (the coherent neutron cross sections of C and S are 5.6 barn and 1.0 barn, respectively,
253 i.e. S contributes less than 9% to the total intensity of the C_2S sample), whereas for x-rays,
254 sulphur ($Z=16$) governs the intensity compared to carbon ($Z=6$) (the scattering power for x-
255 rays is proportional to Z^2). The combined neutron and x-ray data have therefore the potential
256 to pinpoint structural features in quite detail.

257 Figure 6 shows a neutron diffraction pattern of C_2S and compares it to published neutron data
258 of what was called “turbostratic graphite” [23] (the terminology of disordered graphitic
259 systems varies widely between authors). The agreement is remarkable and leaves no doubt
260 on the 2D structure with its sp^2 carbon bonding. A pdf analysis (lower panel) confirms this
261 conclusion: The peaks at 1.41, 2.45, and 2.83 Å, 3.74 Å and 4.24 Å can all be identified with
262 the first four neighbour C-C distances of the 2D honeycomb lattice of graphite or graphene
263 with 2.41 Å edge length. However, one notices the complete absence of a peak at 3.35 Å which
264 would be expected for the inter-layer nearest neighbour C-C distance in graphite. In a
265 diffraction pattern it corresponds to the most intense reflection, the 002.



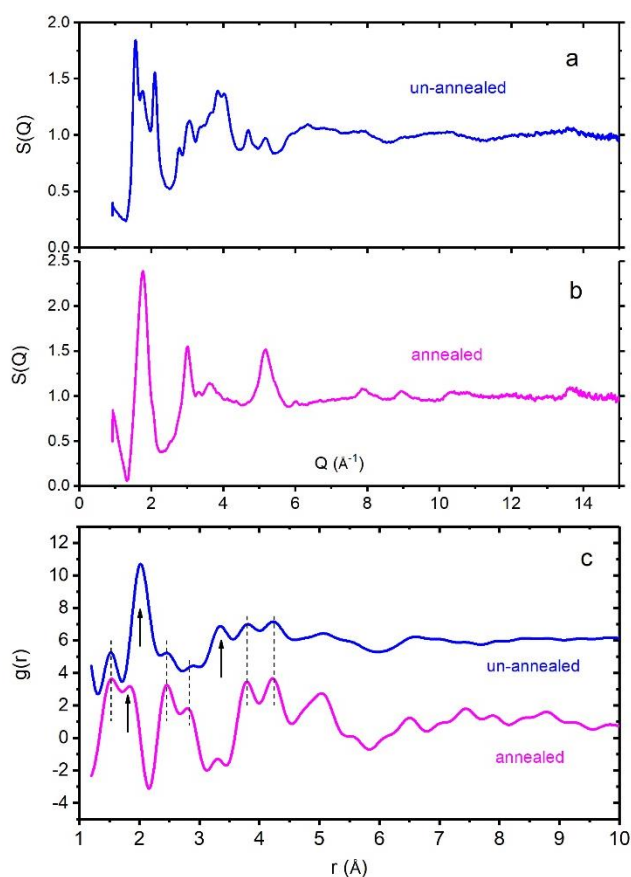
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267 Fig. 6: Neutron diffraction pattern (a) compared to published neutron pattern of “turbostratic
 268 graphite” (b) [23]. The $g(r)$ obtained from pdf analysis of (a) is shown in (c), together with the
 269 geometry in graphite/graphene and its five nearest in-plane carbon-carbon distances.

270

271 Figure 7 shows corresponding x-ray patterns along with a similar pdf analysis. Both patterns
 272 are from the same sample as used in the neutron study, but one pattern was collected after
 273 annealing at 250 °C for 10 h in a vacuum furnace. The difference between the annealed and
 274 the non-annealed sample identifies therefore unambiguously distances relate to sulphur only.
 275 The $g(r)$ of the un-annealed sample shows a strong peak at 2.0 Å followed by a massif of several
 276 peaks between 3 and 5 Å. Other minor peaks, in particular at larger distances, may be artefacts
 277 of the data analysis given the limited Q-range. A comparison with the annealed sample reveals
 278 the disappearance of the most intense peak at 2.0 Å as well as a further peak at 3.3 Å. The

279 remaining peaks are at 1.47 Å, 1.87 Å, 2.43 Å, 2.83 Å, 3.80 Å and 4.24 Å are all – with the
280 exceptions of the 1.87 Å peak – to within ~ 0.05 Å the same as found in the neutron data
281 analysis. This confirms hence once again a hexagonal graphitic lattice.



282
283 Fig. 7: X-ray diffraction pattern of (a) un-annealed and (b) annealed (250°C) samples. The
284 corresponding $g(r)$ obtained from a pdf analysis are shown in (c). The dashed vertical lines
285 indicate distances already identified by neutron diffraction (see Fig. 6) and arrows indicate
286 peaks related to sulphur. The curve for the un-annealed sample was shifted vertically for
287 clarity.

288
289 Beyond any doubt, the two peaks at 2.0 Å and 3.30 Å in $g(r)$ (arrows in Fig. 7c) must be related
290 to sulphur, the fraction which is removed by heating to above 200 °C. The two distances are

291 in fact exactly what one would expect for an S_3 trimer with its well-known 107 degree S-S-S
292 bond angle, a local geometry found in various sulphur allotropes [24]. The peak at 1.87 Å must
293 also be related to sulphur, but to the ~ 10at% fraction which is still present after annealing,
294 and its value corresponds exactly to what is expected for typical covalent C-S bonds. It is this
295 fraction of sulphur which must be responsible for the low-energy Raman modes at 300-400
296 cm^{-1} since these exist even in the annealed samples. Indeed, frequencies in this range are
297 typical for C-S bending modes [25,26].

298 A closer look at the three sharpest features in the diffraction pattern of fig. 7a reveals that
299 their positions agree well with those of “polymeric sulphur” [27], in particular Tuinstra’s
300 “fibrous sulphur” labelled $S_{\omega 1}$ [28,29]. These are highly disordered, non-equilibrium states,
301 usually obtained by quenching sulphur from the liquid and which do not dissolve in carbon
302 disulphide. But in contrast to such reported bulk polymeric sulphur we do not see the
303 associated infrared signature [27] in our samples, nor its decomposition [27] at 120 °C. From
304 this we conclude that the majority of sulphur present in our samples cannot be a separate
305 phase coexisting in a mainly carbon-rich matrix.

306 We have also investigated the electronic properties of un-annealed (C_2S) samples. Fig. 8 shows
307 measurements of the dc-resistivity ρ and its temperature dependence between 5 and 300 K.
308 We find a conductivity ($1/\rho$) of 0.1 $Ohm^{-1}cm^{-1}$ at 300 K which is 13 orders magnitude higher
309 than reported from Bridgman’s black [6]. The compound is a semiconductor. From the slope
310 of the $\ln(\rho)$ vs $1/T$ Arrhenius plot at high temperatures (above 200 K) we derive a gap of 46
311 meV (inset of Fig. 8). At lower temperatures the same presentation deviates significantly from
312 being linear. However, the T-dependence can be well fitted over the entire temperature range
313 by a variable hopping range model [30] given by the expression:

314

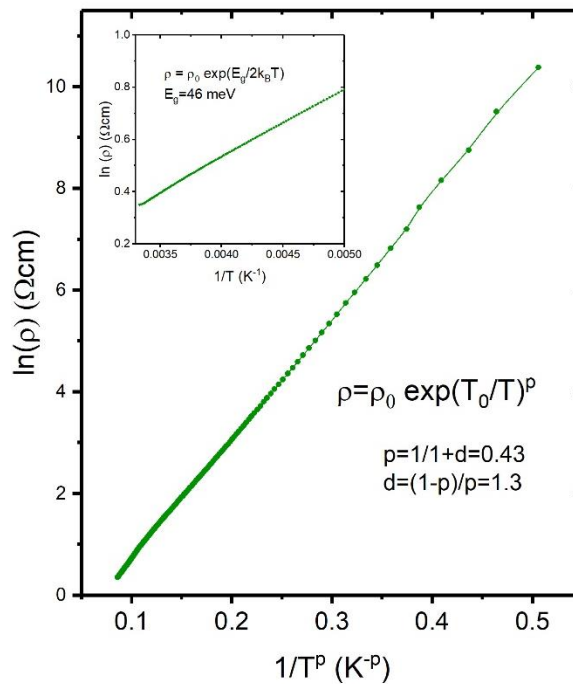
$$\rho = \rho_0 \exp(T_0/T)^p$$

315 where p is a fitting parameter related to the dimension d of the hopping mechanisms by

316 $p=1/(1+d)$. We find $p=0.43$, i.e. $d=1.3$. This appears to be consistent with a structure where

317 short range hopping occurs along a 1-dimensional C-C bond and where hopping over larger

318 distances probe the 2-dimensional nature of the carbon sheets.



319

320 Figure 8: Temperature dependence of resistivity of C_2S . The main picture shows a fit to a

321 variable range hopping model [30], the inset an Arrhenius-plot of the high temperature range

322 to extract the conventional band gap E_g .

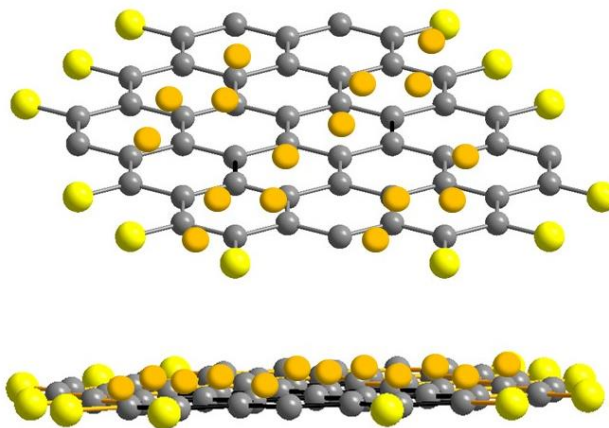
323

324 4. Discussion and conclusion

325 The emerging picture from these studies can hence be resumed as following: When liquid CS_2

326 is compressed at 300 K it crystallizes at 1.3 GPa. Further compression to 7-8 GPa leads to a

327 chemical reaction giving a mixture of pure crystalline sulphur and a compound with
328 nanometric sp^2 -bonded carbon layers, approximate composition of C_2S and a density of $1.76 \pm$
329 0.03 g/cm^3 , see Fig. 9 for an illustration. Most of the sulphur remaining therein is weakly (van
330 der Waals) bonded to the carbon sheets, is locally in form of S_3 trimers with some resemblance
331 to a polymeric state and can be removed by heating to above $200 \text{ }^\circ\text{C}$. The remaining 10 at%
332 sulphur is strongly (covalently) bonded to the carbon backbone and gives rise to Raman modes
333 in the $300\text{-}400 \text{ cm}^{-1}$ range. It persists to temperatures of at least $700 \text{ }^\circ\text{C}$. For chemical reasons,
334 this type of sulphur is most likely bonded to carbon located at the edges of the carbon flakes.
335 Indeed, a flake with 25 \AA diameter (see above) contains approximately 200 carbon atoms from
336 which ~ 30 are on edge positions, i.e. 14%. For a flake with 40 \AA diameter, approximately 10%
337 are on edge positions. In conclusion, given the wide distribution in the size of the flakes, these
338 numbers are consistent with the measured average stoichiometry of $C_{10}S$.



339
340 Fig. 9: Structural model of C_xS : Sulphur is attached to carbon sheets, either by van der Waals
341 bonds (orange atoms) or by covalent bonds (yellow atoms), with average stoichiometry C_2S .
342 Annealing at $T > 200 \text{ }^\circ\text{C}$ removes the van der Waals bonded species, leaving only covalently
343 bonded sulphur resulting in an average composition of $C_{10}S$.

344

345 The question then arises what mechanism leads to the formation of C_xS instead of “Bridgman
346 black” as found in previous 300 K compression studies [8-11]. For this we note that carbon
347 disulphide has a positive formation enthalpy of +88.7 kJ/mole [31], i.e. the molecule is
348 inherently metastable. This contrast with its closest analogue, CO_2 , which has a large negative
349 formation enthalpy of -393 kJ/mol [31]. As a result of this, its polymerisation or partial
350 decomposition is exothermic, and a reaction will self-propagate if the heat cannot be
351 evacuated rapidly. This is likely the case in large-volume pressure apparatuses where the
352 sample surface/volume ratio is small, in contrast to the geometry in diamond anvil cells [8-11]
353 where the anvils, in addition, are excellent heat sinks. The sample in our high pressure method
354 is therefore likely to self-heat to beyond the stability of Bridgman black, potentially into the
355 P/T region which currently is believed to be “carbon+sulphur” [10] or “ CS_2 +sulphur” [9]. If this
356 is correct, our work would mean that in the reaction product so far believed to be simply
357 “carbon” is in fact a new carbon-sulphur compound with stoichiometry C_2S .

358 Finally, this new compound may be compared to other known graphitic compounds. Given
359 the absence of sharp Bragg peaks reminiscent to graphite, in particular the absence of a sharp
360 002 reflection (see above), the compound is not a canonical “graphite intercalated compound”
361 (GIC) in the strict sense. However, C_xS bears some resemblance with graphene oxide, though
362 its structure is fundamentally simpler since it contains only carbon and sulphur with no oxygen
363 functional groups such as hydroxyl. Its closest relative could be a compound termed “RGO/S”
364 [32], judged by the available x-ray, Raman and thermogravimetry data [32]. This is a carbon-
365 sulphur composite obtained by reducing graphene oxide (GO) at 600 °C in sulphur vapour.
366 Since the compound appears to be a promising cathode material for Li-S batteries, our C_xS
367 material might as well be suitable for energy storage devices. Using the high pressure
368 technique applied in this study, the material can be easily produced in cm^3 quantity and –

369 apart from its academic interest - might have interesting other technological application
370 similar to other nanometric 2D graphene-type materials [33,34]. The availability of a material
371 with high surface to weight ratio, with physical properties which can be tailored through its
372 sulphur stoichiometry and which is easily dispersible in an aqueous alcohol solution could find
373 applications for gas sensors, membranes and supercapacitors [33,34].

374

375 **Data Availability.** All data are included in the manuscript and available from the corresponding
376 author upon request and will be deposited on the CNRS cloud <https://mycore.core-cloud.net/>

377

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448

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459

460 **CRedit authorship contribution statement**

461 **S. Klotz:** Writing – original draft, designed the experiment and wrote the paper with
462 contributions from all authors, carried out the Raman and resistivity measurements, produced
463 and prepared all samples. **B. Baptiste:** Formal analysis, carried out the x-ray measurements
464 and the pdf analysis. **T. Hattori:** Formal analysis, carried out the neutron measurements and
465 the pdf analysis. **S.M. Feng:** Produced three samples during a visit of S.K. at IOP Beijing in 2019.
466 **Ch Jin:** Produced three samples during a visit of S.K. at IOP Beijing in 2019. **K. Béneut:** assisted
467 in the Raman and IR measurements. **J.M. Guigner:** carried out the TEM measurements. **I.**
468 **Estève:** carried out the SEM measurements.

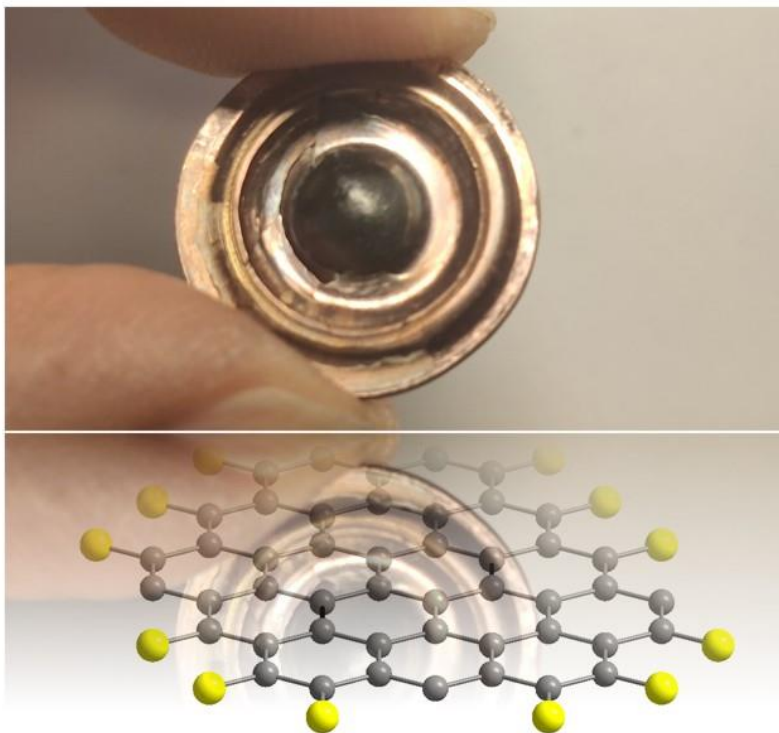
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Graphical abstract

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