

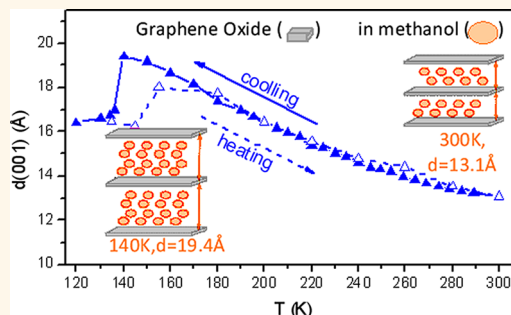
# Enormous Lattice Expansion of Hummers Graphite Oxide in Alcohols at Low Temperatures

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**ABSTRACT** A structural study of swelling of Hummers graphite oxide (H-GO) in excess of liquid alcohols was performed as a function of temperature using synchrotron X-ray diffraction and revealed a strong “negative thermal expansion” effect. The increase of the distance between graphene oxide layers is explained by insertion of additional solvent upon cooling of the H-GO/solvent system. The interlayer distance of H-GO is found to increase gradually upon temperature decrease, reaching 19.4 and 20.6 Å at 140 K for methanol and ethanol, respectively. The gradual expansion of the H-GO lattice upon cooling corresponds to insertion of at least two additional solvent monolayers and can be described as osmotic swelling.

This phenomenon is distinctly different from the solvation of Brodie graphite oxide (B-GO), which was found earlier to exhibit crystalline swelling: single-step insertion of an additional solvent monolayer at low temperatures. The enormous structural expansion of H-GO at low temperatures is suggested to be useful for solution-based intercalation of graphite oxide with relatively large molecules and the synthesis of various composite materials.



**KEYWORDS:** graphite oxide · graphene oxide · solvates · negative thermal expansion · intercalation

Graphite oxide (GO) is a nonstoichiometric material with a layered structure obtained by strong oxidation of graphite.<sup>1–3</sup> Oxidation results in an increase of the interlayer spacing up to  $\sim 6$ – $7$  Å and a transformation of hydrophobic graphite into hydrophilic graphite oxide.<sup>4,5</sup> Interest in studies of GO was revived during the past decade mostly due to the possibility of dispersing it as single sheets in solution, thus producing graphene oxide,<sup>6–12</sup> which can be deposited as thin films, paper-like material, or as a solid membrane.<sup>13–16</sup> Both graphene oxide and graphite oxide can easily be reduced, for example, by chemical or heat treatment.<sup>17–20</sup> However, current interest in graphite oxide goes far beyond graphene synthesis as it demonstrated some unique properties of its own. Graphite oxide is hydrophilic and easily gets intercalated (solvated or swelled) by polar solvents when exposed to vapor or immersed in liquid solvent.<sup>4,5,21,22</sup> The main feature of GO solvation is a significant lattice expansion due to insertion of solvent between oxidized graphene layers.

The unique properties of GO have recently been suggested to have some unusual

applications, such as for fabrication of supercapacitors using laser-induced reductive patterning.<sup>23</sup> Another example of a surprising application of solvated GO was recently suggested by Nair *et al.*,<sup>24</sup> who reported the synthesis and unusual properties of submicrometer-thick membranes made from graphene oxide. The membranes were found to be permeable by water but not by ethanol or other polar solvents. Graphite oxide is also extremely promising for the synthesis of a new generation of sorbent materials with high surface area. The recently reported graphene oxide framework (GOF) materials are synthesized by expansion of the GO structure using intercalation with the proper solvent and a reaction with some organic molecules which link GO planes. The linkers are able to hold the graphene oxide sheets separated when solvent is withdrawn from the structure.<sup>25,26</sup> If a larger separation of graphene oxide layers is achieved in solution, a broader variety of organic linkers can be used for functionalization of graphite oxide.

Our recent experiments with graphite oxide immersed into excess of liquid water revealed the unusual phenomenon

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of “negative thermal expansion”, later demonstrated also for humidity-exposed samples.<sup>27</sup> The GO structure in excess of water shows unique hydration/dehydration behavior upon both temperature and pressure variations.<sup>28,29</sup> Cooling of GO/water samples results first in a *gradual* change of the interlayer spacing in the temperature range of liquid water, with a stepwise contraction at the freezing point of the water medium.<sup>29</sup> This gradual lattice expansion of GO is similar to the *osmotic swelling* known for some clay minerals.

The lattice expansion of GO at lower temperatures is explained by the insertion of additional water from the liquid medium. It is relatively small and occurs only in a short temperature range down to the freezing point of H<sub>2</sub>O.<sup>29</sup> Therefore, it is very interesting to verify if a similar temperature-induced effect of lattice expansion can be found for other solvents which stay liquid in a broader range of temperatures.

Indeed, our previous experiments with GO immersed in methanol and ethanol (melting points of 175 and 159 K, respectively) revealed that insertion of an additional solvent monolayer occurs upon either cooling at ambient pressure or pressure increase at ambient temperature.<sup>28–34</sup> For all tested solvents except water (methanol, ethanol, acetone, dimethylformamide (DMF)), we observed phase transitions into low-temperature (or high-pressure) phases with a stepwise increase of the interlayer distance which correlates to intercalation of an additional monolayer of solvent molecules.<sup>32,34</sup> A similar type of intercalation is known for some clay minerals as *crystalline swelling*.

It should be noted that the properties of graphite oxides synthesized by different methods can be distinctly different.<sup>35</sup> Recent experiments in our group revealed that the crystalline swelling in polar solvents described above appeared to be typical only for graphite oxide synthesized by Brodie’s method. The solvation and hydration properties of GO prepared by Hummers method appeared to be significantly different even at ambient temperature.<sup>36</sup>

Here we present the results of a structural study performed with Hummers graphite oxide (H-GO) in excess of methanol or ethanol, which revealed an enormous lattice expansion upon cooling the systems down to the freezing point of the solvent. An exceptionally strong “negative thermal expansion” allows us to achieve a separation of graphene oxide layers to above 20 Å for ethanol at 130–140 K, compared to ~7 Å separation in the solvent-free graphite oxide structure.

## RESULTS AND DISCUSSION

Powder samples of graphite oxide, synthesized by Hummers method, were loaded into excess of liquid solvent (methanol, ethanol, water) and studied by X-ray diffraction at temperatures below ambient. The results of the experiments performed with H-GO immersed in methanol and ethanol are summarized in

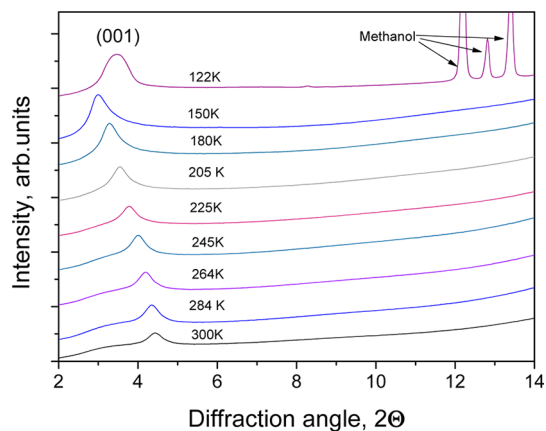


Figure 1. Selected XRD patterns recorded from a H-GO sample in methanol upon cooling. Peaks from solid methanol are shown for the 122 K pattern.

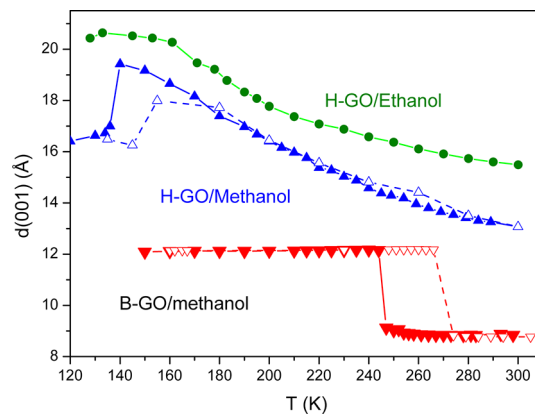
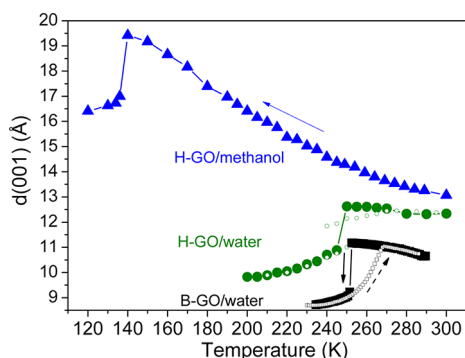


Figure 2. Temperature dependence of the (001) *d*-spacing (corresponding to the distance between graphene oxide layers) for samples of Hummers graphite oxide immersed in excess of methanol (blue) and ethanol (green), as compared with previously reported data for Brodie graphite oxide in methanol (red). Open symbols correspond to data points recorded during sample heating back to room temperature.

Figures 1 and 2. Figure 1 shows selected XRD patterns recorded from a H-GO/methanol sample upon cooling. The structure of H-GO in liquid methanol is turbostratic and very poorly crystalline. A rather weak and broad (001) reflection corresponds to a distance between graphene oxide layers of 13.07 Å at 300 K. Cooling the sample results in a significant shift of the (001) reflection which corresponds to a *gradual* increase of the interlayer distance up to 19.42 Å at 140 K. The temperature evolution of the (001) *d*-spacing is shown in Figure 2. The solidification of liquid methanol observed below 140 K results in a step-like contraction of the H-GO lattice by approximately 2.5 Å. Similar contraction of lattice is observed also at the point of ice formation for GO immersed in water (Figure 3). Experiments with H-GO immersed in ethanol showed qualitatively similar results. A gradual expansion of the H-GO structure was observed upon cooling down to 130 K (reaching



**Figure 3.** Temperature dependence of  $d(001)$  for H-GO/methanol system compared to the B-GO/water and H-GO/water systems. Open symbols correspond to heating samples back to room temperature after initial cooling.

20.64 Å), but the solidification temperature of ethanol was not achieved in this experiment.

The “negative thermal expansion” of graphite oxide in liquid alcohols is, of course, not a purely thermal effect but occurs due to a gradual change in composition of the GO/methanol solvate phase. The expansion of the lattice upon cooling occurs due to insertion of additional solvent from the liquid medium into the GO structure. The composition of the H-GO solvate changes continuously upon cooling, which is in sharp contrast to the low-temperature structural modification reported in our recent study of GO synthesized by Brodie’s method (B-GO) (see Figure 2). In B-GO, insertion of an additional methanol monolayer occurs as a reversible phase transition between two solvated phases with a sharp step change in the interlayer distance by  $\sim 2.5$  Å. The enthalpy of this phase transition was evaluated by DSC in our earlier studies on pure methanol and various methanol–water mixtures.<sup>32</sup> However, a DSC study of H-GO in methanol has not revealed any anomalies typical for phase transitions at low temperatures since insertion of solvent occurs gradually over a broad range of temperatures.

Assuming that insertion of one methanol monolayer results in a lattice expansion by 2.5 Å (as in the phase transition in B-GO, Figure 2), the expansion of the H-GO sample down to 130 K ( $\sim 6$  Å) corresponds to insertion of at least two solvent layers. The maximum separation of the graphene oxide layers in H-GO at 130 K then corresponds to a total amount of four monolayers of solvent. At least one monolayer of solvent is withdrawn from the structure upon solidification of the methanol, which indicates that most of the solvent remains in the interlayer space between graphene oxide sheets. The extremely broad (001) peak of H-GO observed below the freezing point of methanol is most likely explained by an inhomogeneous solvate composition. More than one methanol monolayer could possibly be withdrawn from part of the GO layers, while layers solvated to different degrees are stacked randomly (interstratification).

The phenomenon of a *gradual* shift of the (001) peak position with temperature could possibly be explained by interstratification of layers with different numbers of inserted solvent monolayers and a change in their relative numbers with temperature. Interstratification can sometimes be revealed by the appearance of irrational peaks in the (00l) series. However, H-GO solvated by methanol, ethanol, or water shows only a single reflection for (001) and no higher order reflections. An alternative scenario is insertion of solvent in the liquid-like state controlled by osmotic flow (osmotic swelling). The temperature dependence shown in Figure 2 indicates that at least three monolayers of methanol or ethanol are fixed in the H-GO structure, and the fourth layer is in a more liquid-like state, as follows from its exclusion from the structure upon solidification of the methanol. The exact state of alcohols between graphene oxide layers cannot be verified by XRD. The alcohols are inserted into the H-GO structure in a completely disordered state, and no additional reflections due to solvent insertions are observed after intercalation.

Osmotic swelling of H-GO in ethanol and methanol is qualitatively similar to swelling of both B-GO and H-GO in water, as shown in Figure 3. It is characterized by a gradual increase of the lattice parameter upon cooling and an abrupt contraction of the interlayer distance at the solidification point of the liquid medium by an amount which corresponds to one solvent monolayer. As was demonstrated in earlier studies on liquid immersed<sup>30</sup> and high humidity-exposed samples,<sup>21,22</sup> two kinds of intracrystalline water exist in the highly hydrated GO structure: the first monolayer of water is fixed in the lattice, while with stronger hydration (lattice spacing over 9 Å) water is added in a liquid-like state, in which it shows translational motion along the GO sheets. Liquid-like water escapes from the GO structure at the point of liquid medium solidification, while “crystalline” (but completely disordered) water remains in the lattice even after ice formation. The new results presented here demonstrate that methanol is also inserted into the H-GO structure in two different states: the first 2–3 layers are crystalline (lattice spacing up to  $\sim 16$  Å), while the next layer (over 16 Å) is liquid-like. The fact that a larger amount of methanol can be inserted into the GO structure compared to water is possibly explained by the simple fact that alcohols exist in the liquid state over a much broader range of temperatures and the “negative thermal expansion” thus becomes larger. It should be noted that much stronger hydration of GO can be achieved in slightly alkaline solutions. Layer separations up to  $\sim 22$  Å were observed in our earlier studies of B-GO in alkaline solution upon compression to 1.6 GPa.<sup>33</sup> The “negative compressibility” observed in these experiments under pressure is analogous to the “negative thermal expansion”, which is observed under temperature variations.<sup>29,32</sup>

According to Figures 2 and 3, the H-GO shows osmotic swelling in both water and alcohols. In contrast, B-GO exhibits osmotic swelling when immersed in water and crystalline swelling in alcohols. The Brodie and Hummers methods provide materials which are traditionally given the same name (graphite/graphene oxide) but actually demonstrate rather different properties regarding hydration/solvation. This effect could be attributed to the larger variety of functional groups attached to the graphene oxide sheets in H-GO and the different proportions between the number of C—O—C, C=O, and C—OH groups revealed in our earlier study.<sup>36</sup>

It should also be noted that Hummers method to synthesize GO involves the possibility of contamination by, for example, alkali metals, manganese, or sulfur. However, XPS analysis revealed only small amounts of sulfur and nitrogen impurities, which are unlikely to affect solvation significantly. It is also possible that the very strong oxidation of graphene sheets may result in some defects (*e.g.*, holes in the sheets), which can serve as an additional source of differences between graphite oxides produced by various methods.

The separation of graphene layers by  $\sim 22$  Å achieved by simple cooling of the GO powder immersed in alcohols provides sufficient space for insertion of relatively large molecules and opens new possibilities for synthesis of new graphene-related materials and composites, for example, for synthesis of new graphene oxide frameworks. The size of molecules which could possibly be inserted into the GO lattice using ethanol solution at 140 K is limited to approximately 14 Å, which should be compared to the fact that solvent-free H-GO layers are separated by  $\sim 7.5$  Å. However, further studies will possibly reveal solvents for which the swelling of graphite oxide is even stronger. In this respect, the graphite oxide can be compared to some clay minerals. Clays are a different kind of hydrophilic layered material that exhibit both crystalline and osmotic swelling, showing a lot of similarities with graphite oxides. Intercalation by as many as tens of water monolayers (and layer separations by tens of nanometers) was reported for some clay minerals.<sup>37</sup>

The results presented in this study may also be important for understanding the permeation properties

of graphene oxide membranes reported recently by Nair *et al.*<sup>24</sup> Their micrometer-thick membranes were prepared using Hummers graphite oxide as a precursor, and from a structural point of view, the membrane can be considered as a single graphite oxide flake of macroscopic size. Of course, the properties of such huge flakes can be significantly different compared to finely dispersed powder, which consists of grains a few micrometers in size. However, the hydration and permeation properties of such membranes can be expected to show some similarities with our material as they consist of exactly the same microscopic single layered sheets and even demonstrate similar interlayer distances when hydrated. Therefore, the lattice expansion of the H-GO structure reported in our study at low temperatures will very likely be reflected also in the properties of graphene oxide membranes.

## CONCLUSIONS

In summary, Hummers graphite oxide immersed in liquid alcohols (methanol and ethanol) shows a strong reversible expansion of the lattice upon temperature decrease, thus exhibiting a “negative thermal expansion” phenomenon which is explained by gradual intercalation of solvent into the GO lattice. The maximum distance between the graphene oxide layers is found to be 20.6 Å for the GO/ethanol system at 140 K and corresponds to a solvate phase with at least four monolayers of ethanol. The effect is specific only to Hummers graphite oxide and is distinctly different from the phase transitions observed at low temperature for Brodie graphite oxide. It can be concluded that the properties of graphite oxides, especially with respect to hydration/solvation, should always be correlated with the particular synthesis methods used. The enormous separation of the GO layers in methanol or ethanol solvates at low temperatures opens new possibilities for functionalization or intercalation of graphene oxide with larger molecules and the synthesis of new graphene oxide framework materials. The gradual expansion of the GO lattice also provides an opportunity for applications as a molecular sieve with variable pore size tuned by temperature.

## METHODS

Commercial GO produced by Hummers method was purchased from ACS Material, USA. Detailed characterization of this sample by XPS, Raman, and FTIR spectroscopy was reported in our earlier study.<sup>36</sup> The C/O ratio of 2.47 was determined by XPS and excludes water since it was measured on a dried sample at high vacuum conditions. Elemental analysis showed no contamination with alkali metals (K, Na) or Mn, typical contaminations specific to Hummers method of synthesis. However, a relatively small contamination with nitrogen (1.7 at. %) and sulfur (0.7 at. %) was detected. *In situ* synchrotron radiation XRD

cooling experiments (from room temperature down to about 150 K) were performed at the Max-Lab III beamline I711, Sweden. X-ray diffraction images were collected from powder samples loaded in glass capillaries with excess amounts of solvent using the transmission geometry. Temperature was controlled by an Oxford Cryosystems CryoStream 700+ cooler and decreased/increased in steps of 3–10 K. The radiation wavelength (1.0090 Å) was calibrated using a LaB<sub>6</sub> standard. Fit2D software was used to integrate the diffraction images into diffraction patterns.

*Conflict of Interest:* The authors declare no competing financial interest.

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