

Phase Transitions in Graphite Oxide Solvates at Temperatures Near Ambient

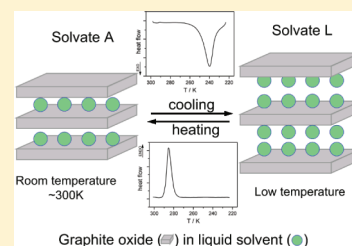
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Supporting Information

ABSTRACT: It is demonstrated that solvent-saturated graphite oxide can be considered to be solid solvate, and two phases with distinctly different solvent composition are found near room temperature. Phase transitions between these two solvated phases were observed using synchrotron powder X-ray diffraction and DSC for methanol, ethanol, acetone, and dimethylformamide (DMF) solvents. Solvate A, formed at room temperature, undergoes a reversible phase transition into expanded Solvate L at temperatures slightly below ambient due to insertion of one monolayer of solvent molecules between the GO planes. The phase transition is reversible upon heating, whereas the low-temperature expanded phase L can be quenched to room temperature for ethanol and DMF solvents.

SECTION: Nanoparticles and Nanostructures



Graphite oxide (GO) is a nonstoichiometric material obtained by strong oxidation of graphite.^{1–3} In the past few years, it has attracted much attention, for example, as a precursor for the synthesis of graphene and graphene-related materials,^{4–9} as a material for supercapacitors,¹⁰ and as photocatalyst for hydrogen production from water.¹¹ GO has a layered structure similar to pristine graphite but strongly disordered. Attachment of oxygen and –OH groups to the graphene layers results in some buckling of planes, and the interlayer spacing increases to ~ 6 Å.^{12–14} The structure of GO depends on the particular method used and the degree of oxidation which makes precise structure definition somewhat uncertain despite recent strong research efforts.^{15–19} GO is hydrophilic and is easily hydrated when exposed to humid air or liquid water with a further increase in the interlayer distance up to ~ 12 Å.^{15,18,19} The insertion of water (and other polar solvents) should be considered to be intercalation of GO and the corresponding structures as solid solvates. However, they are stable only when immersed in solution and rapidly desolvated in air. A better understanding of the properties of GO immersed in water and other solvents is rather important for the development of solution-based GO chemistry,^{20–22} for the reduction of GO to graphene,^{23,24} and for various technological applications.^{10,25–27}

Recently, we revealed that solvates of GO with water, methanol, ethanol, and acetone exhibit anomalies connected to insertion of additional solvent into the structure when pressurized in an excess of liquid solvent.^{28–31} An anomalous gradual structural breathing due to insertion/desertion of liquid water was observed in the GO/water system upon both pressure and temperature variations.^{28,32} For methanol, ethanol, and acetone, an increase of pressure resulted in reversible phase transitions (at 0.3 to 0.8 GPa) into new expanded phases with interlayer distance increase corresponding to insertion of one monolayer of the corresponding solvent.^{29,31} It is not

uncommon that phase transitions observed upon a pressure increase can also be found under ambient pressure conditions upon cooling, for example, ref 33. Phase transitions connected to insertion/desertion of solvent at ambient pressures would be, of course, of much more general importance because the high-pressure studies remain to be relatively exotic and typically performed on rather small samples. In contrast, structural variations upon temperature change are extremely important and must be taken into account in any solution-based chemistry of GO, in the dispersion of GO on single layers performed in solution, in solution-based methods of GO reduction into graphene, and so on.

Here we demonstrate that temperature variations imposed on the GO immersed in excess amounts of several polar solvents (methanol, ethanol, acetone, dimethylformamide (DMF)) result in lattice expansion/contraction, which correspond to insertion/desertion of solvent monolayer. The solvent-saturated GO can be considered to be a solid solvate, whereas two phases with distinctly different solvent composition exist near room temperature. Reversible phase transitions between two solvate phases were observed upon temperature variations.

Results and Discussion. A detailed temperature-dependent structural study was first performed for GO powder immersed in excess amounts of methanol and ethanol. The structural transformations were monitored using in situ synchrotron X-ray diffraction in glass capillaries and verified by differential scanning calorimetry (DSC). Additional experiments were then performed with GO/acetone and GO/DMF, as described below.

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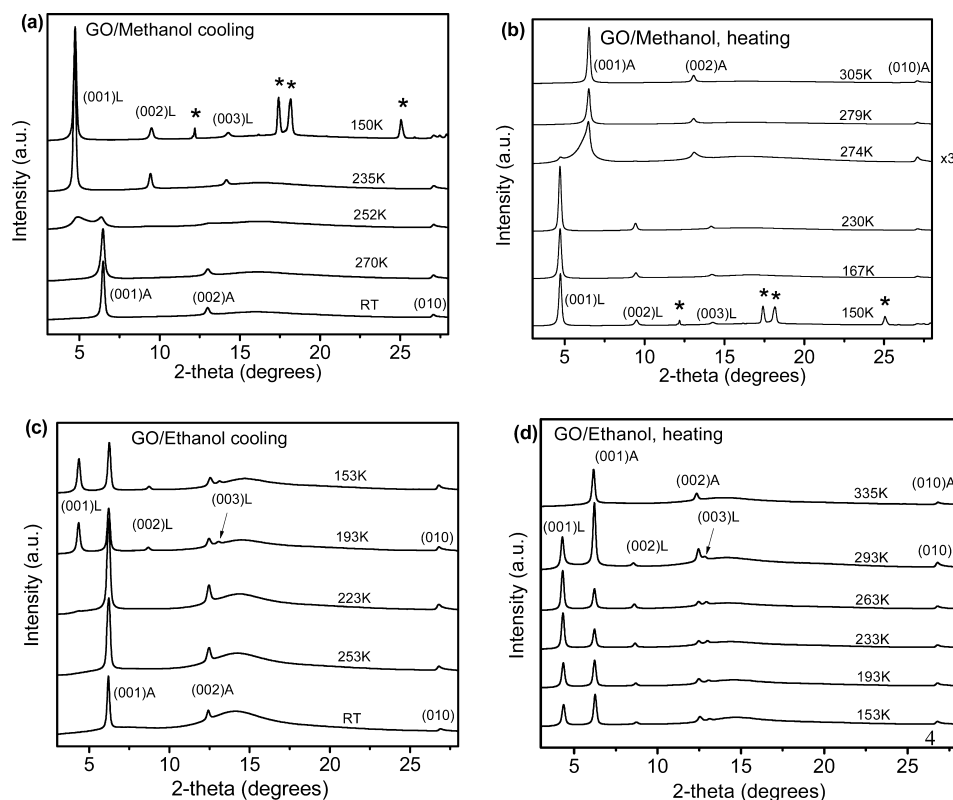


Figure 1. XRD patterns ($\lambda = 0.99874 \text{ \AA}$) recorded upon cooling and consequently heating of GO/methanol sample (a,b) and GO/ethanol sample (c,d). The stars in panels a and b indicate diffraction lines from frozen solid methanol. Indexing of the GO solvates reflections: A refers to ambient solvate phases observed in the room-temperature pattern; L refers to the low-temperature expanded solvate phases. The broad feature around $13\text{--}16^\circ$ is mostly from liquid solvent (Figure 1s in the Supporting Information).

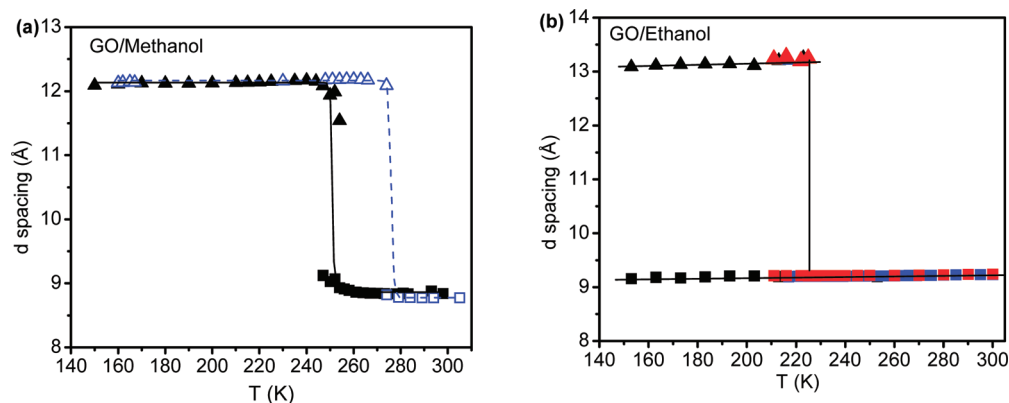


Figure 2. Temperature dependence of (001) d spacings for GO dispersed in excess of (a) methanol and (b) ethanol. Solid and open symbols represent d spacings during cooling and heating, respectively, squares represent d spacings of the ambient phase, and triangles represent those of the low-temperature phase. Black, blue, and red symbols in panel b represent data from separate runs.

In agreement with previously published data, GO powder immersed in an excess of liquid alcohols forms expanded solvate phases.²⁹ The interlayer distance of GO increases to 8.84 \AA in methanol and to 9.24 \AA in ethanol, compared with $\sim 6.6 \text{ \AA}$ for the solvent free state, and corresponds to insertion (intercalation) of approximately one monolayer of solvent into the GO structure.

Cooling of the GO/methanol sample resulted in a clear phase transition at $253\text{--}254 \text{ K}$, as shown in Figure 1a,b. Below this temperature, diffraction peaks from the ambient phase (solvate A) are replaced with peaks from an expanded solvate phase with the interlayer distance increased by $\sim 3.3 \text{ \AA}$ (solvate

L). The XRD pattern recorded at 252 K (Figure 1a) shows a point of transition where both phases were simultaneously observed. The solvate L phase was stable upon further cooling, and no structural transformations were observed, even at the point of methanol freezing at 150 K , which is ca. 25 K lower than the freezing point of pure methanol.

The phase transition is reversible, and upon heating the ambient phase was recovered above 270 K (Figure 1b). The temperature dependence of the (001) d spacing shown in Figure 2a reveals a temperature hysteresis typical for reversible first-order phase transitions. The corresponding dependence of fwhm of the (001) reflection in Figure 3 shows strong

variations in a narrow temperature interval near the phase transitions.

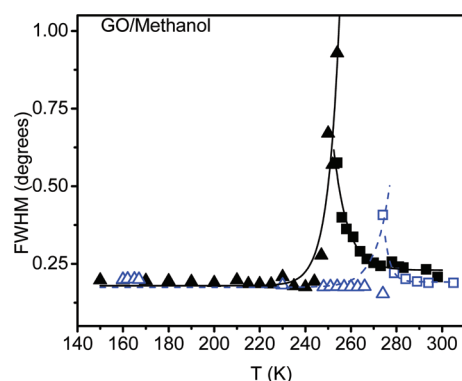


Figure 3. fwhm of (001) reflection for GO/methanol at different temperatures. Solid and open symbols represent d spacings observed during cooling and heating, respectively; squares represent d spacings of ambient phases and triangles represent d spacings of low-temperature phases.

The step-like change in the interlayer distance of the GO observed in Figure 2 is expected if the phase transition corresponds to intercalation of an additional layer of methanol molecules between GO planes. The increase in the separation of layers (3.3 Å) corresponds to the size of the methanol molecule.

Similar phase transitions were found also for GO immersed in an excess amount of ethanol (Figure 1c,d). However, only part of the material transformed into an expanded solvated phase at low temperatures. This behavior is identical to that observed at our previously published pressure-induced insertion of ethanol into the GO structure, and we attributed this to the larger size of the ethanol molecule (insertion more difficult) and to the inhomogeneous nature of the GO sample.²⁹ The A solvate to L solvate phase transition of GO/ethanol was found to occur at 223 K upon cooling, whereas both phases coexisted down to 153 K, the lowest temperature reached in the experiment. The expanded L phase appeared to be more stable compared with that in the GO/methanol system and desolvated back to ambient phase only upon heating above room temperature to 325 K (Figures 1d and 2b).

The phase transitions revealed by XRD were also confirmed using DSC, which provided estimation of enthalpy change due to insertion/desertion of solvent monolayer. Results of DSC experiments with samples of GO immersed in several solvents are shown in Figure 4, and all results are summarized in Table 1. The best quality of the data was obtained for the GO/

Table 1. Summary of Data Related to Phase Transitions between A and L Solvates of GO^a

	T_{on} (K)	T_{m} (K)	ΔH (J/g)	Δd (001) (Å)	P_{onset} (GPa)
GO/methanol	279	285	11.45	3.3	0.4
GO/ethanol				4.1	0.6
GO/acetone	268	272	7.76	3.9	0.8
GO/DMF	308	315	7.33	4.4	<0.2

^aColumn content from left to right: T_{on} : onset temperatures for the transition of solvate L (low temperature expanded structure) to A (ambient phase); T_{m} : temperature for the endothermic peak maximum for the same transition; ΔH : enthalpy difference measured for the transition from solvate L to solvate A on heating; difference in (001) d spacing between solvates L and A; pressure points for similar phase transitions observed in our previous high-pressure ambient temperature experiments.^{29,31} For DMF the pressure point of transition refers to previously unpublished data as the expanded phase was already found at the first pressure point (0.2 GPa).

methanol system, which exhibited a very clear and sharp exothermic peak starting at ~250 K on cooling (Figure 4b, corresponding to solvent insertion and formation of an expanded L phase) and an endothermic peak with onset at 279 K on heating (loss of solvent and transition into the A solvate), all in good agreement with the XRD data.

Experiments with ethanol showed no well-resolved peaks, most likely due to incomplete and gradual transformation between A and L solvates. (See Figure 1.) Experiments with the GO/methanol system proved that DSC could be used as an easy test for the existence of phase transitions between solvate phases of GO. Therefore, we made additional experiments with GO immersed in acetone and DMF.

DSC traces recorded for GO/acetone and GO/DMF samples showed very broad and poorly visible anomalies on cooling but very clear transitions back to the ambient A solvate on heating (Figure 4).

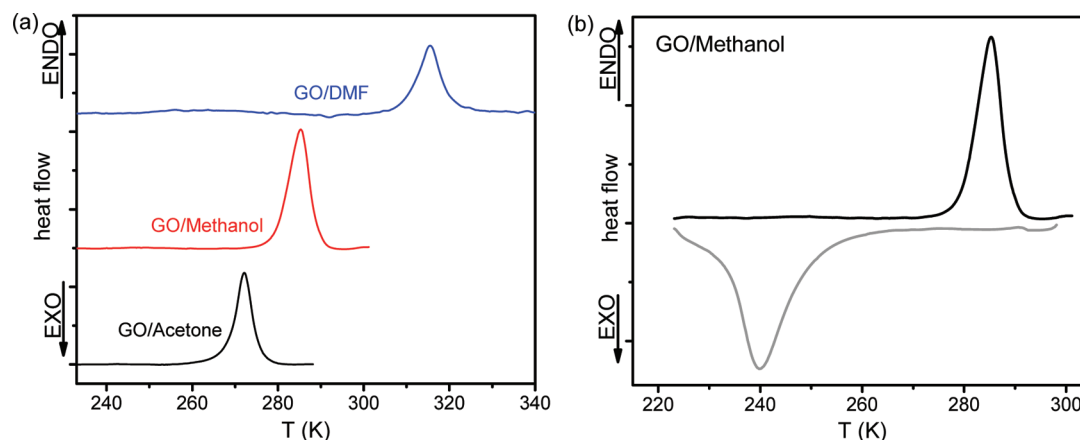


Figure 4. (a) DSC curves for GO immersed in excess amounts of different solvents upon heating with a scanning rate 10 K/min. (b) Full cycle with cooling and heating parts recorded for a GO/methanol sample.

The enthalpies ΔH observed for the phase transitions are summarized in Table 1. The highest value was obtained for methanol (11.45 J/g considering the weight of solvent-free GO powder loaded in the experiment) and smaller for other solvents. The phase transition can be described using the following equation

$$\begin{aligned} \text{GO} \bullet [n \times \text{solvent}] \\ = \text{GO} \bullet [m \times \text{solvent}] + (n - m) \times \text{solvent} + \Delta H_{\text{sol}} \end{aligned} \quad (1)$$

where m is the number of solvent molecules in the A solvate and n is the number of solvent molecules in the L solvate.

Similar desolvation transitions are known for many methanol solvates formed with organic molecules. For example, desolvation of methanol solvate of spironolactone (organic molecule somewhat resembling a “molecule” of GO) was found in ref 34 to result in an enthalpy change of 11.9 J/g, very similar to our result.

The absence of sharp anomalies for DMF and acetone on cooling we attribute to slow kinetics of solvent insertion in these phase transitions, which occur over broad intervals of temperature. Nevertheless, the fact of solvate L formation is clearly proven by sharp anomalies due to desolvation, which was observed on the DSC trace (Figure 5) at a temperature

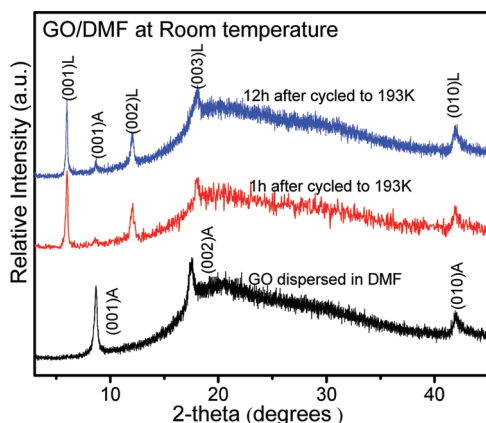


Figure 5. X-ray diffraction patterns recorded using conventional diffractometer ($\lambda = 1.5406$ nm): bottom curve is from pristine GO powder dispersed in excess DMF solvent loaded in glass capillary; middle and top: XRD of the same capillary filled with GO and DMF solvent after cooled to 193 K and heated and exposed to room temperature for different time periods. Indexing of the GO solvate reflections: A refers to ambient solvate phases observed in the room-temperature pattern; L refers to the low-temperature expanded solvate phases.

that is slightly above ambient. This result proves that the L solvate obtained at low temperatures must be stable when heated back to room temperature, which was easy to verify using XRD. The XRD patterns of GO/DMF were first recorded in a glass capillary at ambient temperature, showing reflections from the A solvate; then, the sample was placed in a freezer at 193 K for several hours. As expected, the A solvate transformed into the expanded L solvate at low temperatures, and this phase was observed when the sample heated back to room temperature. XRD patterns recorded from this sample (Figure 5 and Figure 2s in the Supporting Information) revealed that the L solvate phase was preserved even after tens of hours of exposure to ambient temperatures.

For the GO/ethanol sample, DSC revealed no sharp peaks either on cooling or on heating. Only some small changes in the slopes of the curves were observed, which is expected if both insertion and desorption of the solvent is slow. The phase transition was clearly only partial also according to the XRD data presented above, with both solvated phases coexisting over broad interval of temperatures. The A solvate of GO/ethanol was recovered after a cooling run only when the sample was heated to 335 K, above room temperature. Once again, this result correlates well with our high-pressure experiments that showed that the phase transition in the GO/ethanol system was incomplete, whereas the high-pressure phase (which correlated with the L solvate formed at low temperatures) could be quenched upon complete pressure release.²⁹

As shown in Table 1, the temperature points of phase transitions between the A and L solvate phases of GO observed upon temperature variations correlate well with similar transitions observed at high pressure for all studied solvents.^{29,31} Higher pressures required for the formation of expanded solvate correlate with lower temperatures when the same transition is achieved by temperature variation (Table 1). It can be concluded that the nature of the phase transitions observed upon pressure increase is the same as that observed for a temperature decrease and is connected to insertion of one monolayer of solvent.

Observation of phase transitions between solvated phases of GO upon temperature variations has much broader practical and technical importance than the corresponding observations under relatively exotic gigapascal pressure conditions. The structural changes observed in GO/solvent samples upon temperature variations should be very important for a broad range of chemical functionalization and reduction reactions usually performed in solution.^{20–27,38} It is very interesting also that the expanded solvate phases of GO with ethanol and DMF can easily be prepared by exposing samples to low temperature and then studied at ambient room temperature.

In principle, phase transitions between two different solvate states are not uncommon. A well-known example that has recently attracted much attention is C_{60} solvates with nonpolar solvents. The phase transitions observed for C_{60} immersed, for example, in aromatic solvents were studied extensively during the past decade using both XRD and DSC.^{35–37} However, the C_{60} structure is molecular, not layered, and incorporation of additional solvent at low temperatures resulted in lowering the symmetry of the unit cell. In contrast, GO undergoes isostructural phase transitions between two solvated phases with different amounts of intercalated solvent.

It is interesting to note that the existence of solvates, for example, in C_{60} -solvent systems, results in a change of slope of the temperature dependence of solubility.³⁷ GO is not directly soluble in related solvents as it is composed of micrometer size planar sheets. However, it is also well known that GO can be dispersed in various solvents as separate graphene-like sheets using, for example, slightly basic water or strong sonication. Therefore, it is very likely that solvation (and solubility) of GO “molecules” (single sheets) will be affected by temperature variations and their interactions with solvent will be different below and above the phase transition points found in our study.

In conclusion, GO immersed in excess amounts of methanol, ethanol, acetone, and DMF undergoes reversible phase transitions upon cooling to temperatures slightly below ambient. It is demonstrated that the ambient temperature and low-temperature phases of GO can be considered as solid

solvate phases with the amount of solvent different by one monolayer. The phase transition was revealed by X-ray diffraction, whereas the enthalpy for insertion/desertion of a solvent monolayer was evaluated using DSC. The strong temperature hysteresis observed for phase transition in GO/DMF and GO/ethanol systems allows us to quench low-temperature expanded solvate L phase to ambient temperatures. Our results are of general importance for solution-based chemistry of GO including dispersion of GO on single-layer flakes, reduction into graphene, functionalization of GO in solution, and so on.

■ EXPERIMENTAL SECTION

The GO sample was prepared by Brodie's method, and details of synthesis and characterization are described elsewhere.²⁸ X-ray diffraction images were collected from powder samples upon cooling/heating starting from room temperature down to ~150 K at the Max-lab III beamline I711, Sweden. Experiments were performed with glass capillaries filled with GO powder and excess amounts of methanol/ethanol in transmission geometry. Temperature was controlled by an Oxford Cryosystems CryoStream 700+ cooler and decreased/increased in steps of 3–10 K. The radiation wavelength (0.99874 Å) was calibrated using a LaB₆ standard. Fit2D software was employed to integrate the diffraction images into diffraction patterns. The XRD pattern of GO/DMF sample was recorded using a conventional diffractometer with $\lambda = 1.542$ nm.

Differential scanning calorimetry was employed to monitor the heat effect of the phase transformations. GO powder and excess amount of solvent (e.g., 2.0 mg GO in 12.7 mg methanol) was loaded into sealed aluminum sample capsules of ca. 50 μ L volume. The temperature was programmed to change at a 10 K/min rate on both cooling and heating. The samples were first cooled from room temperature to ~213 K and then heated.

■ ASSOCIATED CONTENT

Supporting Information

XRD pattern recorded from empty glass capillary, ethanol-filled capillary, and GO/DMF solvate. This material is available free of charge via the Internet <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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