

1: Graphite - Wikipedia

The research on graphite intercalation compounds often acts as a forerunner for research in other sciences. For instance, the concept of staging, which is fundamental to graphite intercalation compounds, is also relevant to surface science in connection with adsorbates on metal surfaces and to high.

Open in a separate window We present detailed multifrequency resonant Raman measurements of potassium graphite intercalation compounds GICs. From a well-controlled and consecutive in situ intercalation and high-temperature deintercalation approach the response of each stage up to stage VI is identified. The positions of the G and 2D lines as a function of staging depend on the charge transfer from K to the graphite layers and on the lattice expansion. Ab initio calculations of the density and the electronic band structure demonstrate that most but not all of the transferred charge remains on the graphene sheets adjacent to the intercalant layers. Thus, higher stage GICs offer the possibility to measure the vibrations of single, double, and multilayer graphene under conditions of biaxial strain. This strain can additionally be correlated to the in-plane lattice constants of GICs determined by X-ray diffraction. The outcome of this study demonstrates that Raman spectroscopy is a very powerful tool to identify local internal strain in pristine and weakly charged single and few-layer graphene and their composites, yielding even absolute lattice constants. Graphite intercalation compounds GICs consist of a consecutive stacking of graphene layers with intercalated alkali metals, alkali earth metals, or rare-earth elements as well as p-type dopands like FeCl₃, AsF₅, or H₂SO₄ in between. The electronic band structure, charge transfer of different alkali stage I GICs, was also directly measured by photoemission spectroscopy ²², ²³ and recently with more accuracy for the full Fermi surface, quasiparticle band structure, and Dirac cone in KC₈. Combination of the reflectivity spectra of alkali GIC up to stage IV with such calculation revealed a good agreement. To highlight the importance of the charge transfer, we will refer to them in the following as charged c and uncharged uc layers. The higher frequency line at about cm^{-1} , which is present for all stages, was consequently ascribed to the c layers, even though the exact mechanism of the stiffening remained unclear at the time. The stiffening has by now been understood as the effect of nonadiabaticity onto the vibrations of charged graphene layers ³² and ab initio calculations of stage I GICs have indeed confirmed the strong blue-shift of the G-line. However, the model alone is not able to explain the subtle frequency shifts of the G-line for the different stages and has not yet been used to investigate the dependence of the 2D line on staging. In this report, we present an extensive Raman spectroscopy study of potassium GICs, measuring both the G and the 2D lines for different laser energies and for the different intercalation stages up to stage VI. The measurements are accompanied by ab initio calculations of the electronic structure, charge transfer, lattice expansion, and vibrational properties of these GICs. We present a quantitative refinement of the nearest layer model which takes into account the exact charge transfer, the lattice expansion, and the effect of AB-stacking of the inner uc layers. By comparing our results with the available experimental data on charged, strained, and multistacked graphene layers, we show how to disentangle the different partially counteracting effects onto the position of the Raman lines. We will show that this has important implications for the application of Raman spectroscopy to identify, for instance, the strain in nanocarbon-based nanoelectronic and optoelectronic devices as well as the local interfacial strain in graphene and carbon nanotube polymer composites on an absolute scale. Then we performed controlled temperature-driven deintercalation experiments to synthesize the higher intercalation stages: The G-line always displays a high frequency component G_c between and cm^{-1} . This mode has a slight asymmetry due to the Fano interference of the conduction electrons in the electron-doped charged layers, and it is related to the charged graphene layers next to an intercalant layer. This assignment is also confirmed by comparison to stage II KC₂₄, where each graphene layer is in contact with potassium atoms and only charged graphene layers exist. Hence, KC₂₄ exhibits only one G-line as G_c at cm^{-1} . In addition, for stages higher than KC₂₄ a second line G_{uc} appears around cm^{-1} . The position of the G_{uc} is close to the G-line in pristine graphite cm^{-1} and of graphene 34 cm^{-1} . Therefore, G_{uc} is assigned to the response of basically uncharged graphene layers surrounded by charged graphene layers. A detailed line shape analysis of the two G-line

components using an asymmetric Fano line for the charged layers G_c next to an intercalant layer and a Lorentzian line for the uncharged carbon layers G_{uc} was performed. This shift is not predicted by the NL model. We will explain the shift below in an analysis that takes into account the small fractional charging even of the inner layers and the lattice expansion due to intercalation.

2: Graphite intercalation compound - Wikipedia

The research on graphite intercalation compounds often acts as a forerunner for research in other sciences. For instance, the concept of staging, which is fundamental to graphite intercalation compounds, is also relevant to surface science in connection with adsorbates on metal surfaces and to high-temperature superconducting oxide layer materials.

These materials are prepared by treating graphite with a strong oxidant or a strong reducing agent: The host graphite and the guest X interact by charge transfer. An analogous process is the basis of commercial lithium-ion batteries. In a graphite intercalation compound not every layer is necessarily occupied by guests. In so-called stage 1 compounds, graphite layers and intercalated layers alternate and in stage 2 compounds, two graphite layers with no guest material in between alternate with an intercalated layer. The actual composition may vary and therefore these compounds are an example of non-stoichiometric compounds. It is customary to specify the composition together with the stage. The layers are pushed apart upon incorporation of the guest ions. Examples[edit] Alkali and alkaline earth derivatives[edit] Potassium graphite under argon in a Schlenk flask. A glass-coated magnetic stir bar is also present. One of the best studied graphite intercalation compounds, KC₈, is prepared by melting potassium over graphite powder. The potassium is absorbed into the graphite and the material changes color from black to bronze. The bond between anionic graphite layers and potassium cations is ionic. The crystal structure of CaC₆ belongs to the R3m space group. The graphite interlayer distance increases upon Ca intercalation from 3. Different from other alkali metals, the amount of Na intercalation is very small. Quantum-mechanical calculations show that this originate from a quite general phenomenon: Graphite bisulfate, perchlorate, hexafluoroarsenate: In contrast to the potassium and calcium graphites, the carbon layers are oxidized in this process: Cathodic reduction of graphite perchlorate is analogous to heating KC₈, which leads to a sequential elimination of HClO₄. Both graphite bisulfate and graphite perchlorate are better conductors as compared to graphite, as predicted by using a positive-hole mechanism. The chloride derivatives have been most extensively studied. As the stage number increases the interaction between spins in successive magnetic layers becomes weaker and 2D magnetic behaviour may arise. Halogen- and oxide-graphite compounds[edit] Chlorine and bromine reversibly intercalate into graphite. In the case of bromine, the following stoichiometries are known: Because it forms irreversibly, carbon monofluoride is often not classified as an intercalation compound. It has the formula CF_x. The color is greyish, white, or yellow. The bond between the carbon and fluorine atoms is covalent. Tetracarbon monofluoride C₄F is prepared by treating graphite with a mixture of fluorine and hydrogen fluoride at room temperature. The compound has a blackish-blue color. Carbon monofluoride is not electrically conductive. It has been studied as a cathode material in one type of primary non-rechargeable lithium batteries. Graphite oxide is an unstable yellow solid. Properties and applications[edit] Graphite intercalation compounds have fascinated materials scientists for many years owing to their diverse electronic and electrical properties. KC₈[edit] The bronze-colored material KC₈ is one of the strongest reducing agents known. It has also been used as a catalyst in polymerizations and as a coupling reagent for aryl halides to biphenyls. A new essential application for potassium graphite was introduced by the invention of the potassium-ion battery. Like the lithium-ion battery, the potassium-ion battery should use a carbon-based anode instead of a metallic anode. In this circumstance, the stable structure of potassium graphite is an important advantage.

3: Graphite Intercalation Compounds II : Hartmut Zabel :

This book covers the basic physics and materials science of graphite intercalation compounds. The emphasis is on the layered or quasi-two-dimensional structure of these compounds, which provides an exciting arena for testing physical concepts in lower dimensions.

It can conduct electricity due to the vast electron delocalization within the carbon layers a phenomenon called aromaticity. These valence electrons are free to move, so are able to conduct electricity. However, the electricity is primarily conducted within the plane of the layers. The conductive properties of powdered graphite [16] allow its use as pressure sensor in carbon microphones. Graphite and graphite powder are valued in industrial applications for their self-lubricating and dry lubricating properties. This hypothesis has been refuted by studies showing that air and water are not absorbed. The use of graphite is limited by its tendency to facilitate pitting corrosion in some stainless steel, [20] [21] and to promote galvanic corrosion between dissimilar metals due to its electrical conductivity. It is also corrosive to aluminium in the presence of moisture. For this reason, the US Air Force banned its use as a lubricant in aluminium aircraft, [22] and discouraged its use in aluminium-containing automatic weapons. It is sometimes called white graphite, due to its similar properties. When a large number of crystallographic defects bind these planes together, graphite loses its lubrication properties and becomes what is known as pyrolytic graphite. It is also highly anisotropic, and diamagnetic, thus it will float in mid-air above a strong magnet. Pyrolytic graphite and pyrolytic carbon are often confused but are very different materials. This particular deposit of graphite was extremely pure and soft, and could easily be cut into sticks. Because of its military importance, this unique mine and its production were strictly controlled by the Crown. The Dixon pencil is still in production. In 1789, the German Society of Mining Engineers and Metallurgists organized a special symposium dedicated to their discovery and, thus, the 100th anniversary of flotation. The Bessel process was limited in use, primarily because of the abundant cleaner deposits found around the globe, which needed not much more than hand-sorting to gather the pure graphite. The state of the art, ca. 1800. Both of these names arise from confusion with the similar-appearing lead ores, particularly galena. The Latin word for lead, plumbum, gave its name to the English term for this grey metallic-sheened mineral and even to the leadworts or plumbagos, plants with flowers that resemble this colour. The term black lead usually refers to a powdered or processed graphite, matte black in color. Abraham Gottlob Werner coined the name graphite "writing stone" in 1789. He attempted to clear up the confusion between molybdena, plumbago and black lead after Carl Wilhelm Scheele in 1781 proved that there are at least three different minerals. However, the process of separating it from graphite will require more technological development. Refractories[edit] The use of graphite as a refractory material began before with the graphite crucible used to hold molten metal; this is now a minor part of refractories. In the 1800s, the carbon- magnesite brick became important, and a bit later the alumina-graphite shape. As of [update] the order of importance is: Crucibles began using very large flake graphite, and carbon-magnesite brick requiring not quite so large flake graphite; for these and others there is now much more flexibility in the size of flake required, and amorphous graphite is no longer restricted to low-end refractories. Alumina-graphite shapes are used as continuous casting ware, such as nozzles and troughs, to convey the molten steel from ladle to mold, and carbon magnesite bricks line steel converters and electric-arc furnaces to withstand extreme temperatures. Graphite blocks are also used in parts of blast furnace linings where the high thermal conductivity of the graphite is critical. High-purity monolithics are often used as a continuous furnace lining instead of carbon-magnesite bricks. The US and European refractories industry had a crisis in the 1970s, with an indifferent market for steel and a declining refractory consumption per tonne of steel underlying firm buyouts and many plant closures. Since much of the lost capacity was for carbon-magnesite brick, graphite consumption within the refractories area moved towards alumina-graphite shapes and monolithics, and away from brick. The major source of carbon-magnesite brick is now imports from China. Natural and synthetic graphite are used to construct electrodes in major battery technologies. Laptops, mobile phones, tablets, and smartphone products have increased the demand for batteries. Electric-vehicle batteries are anticipated[by whom? Steelmaking[edit]

Natural graphite in steelmaking mostly goes into raising the carbon content in molten steel, and can also be used to lubricate the dies used to extrude hot steel. Carbon additives are subject to competitive pricing from alternatives such as synthetic graphite powder, petroleum coke, and other forms of carbon. A carbon raiser is added to increase the carbon content of the steel to the specified level. A brake-lining industry shake-out with some plant closures has not been beneficial, nor has an indifferent automotive market. Painting the inside of a mold with it and letting it dry leaves a fine graphite coat that will ease separation of the object cast after the hot metal has cooled. Graphite lubricants are specialty items for use at very high or very low temperatures, as forging die lubricant, an antiseize agent, a gear lubricant for mining machinery, and to lubricate locks. Having low-grit graphite, or even better, no-grit graphite ultra high purity, is highly desirable. It can be used as a dry powder, in water or oil, or as colloidal graphite a permanent suspension in a liquid. An estimate based on USGS graphite consumption statistics indicates that 2, tonnes was used in this fashion in It stems from graphein, meaning to write or draw in Ancient Greek. Plumbago is another older term for natural graphite used for drawing, typically as a lump of the mineral without a wood casing. The term plumbago drawing is normally restricted to 17th and 18th century works, mostly portraits. Today, pencils are still a small but significant market for natural graphite. Graphite of various hardness or softness results in different qualities and tones when used as an artistic medium. The expanded graphite can be used to make graphite foil or used directly as "hot top" compound to insulate molten metal in a ladle or red-hot steel ingots and decrease heat loss, or as firestops fitted around a fire door or in sheet metal collars surrounding plastic pipe during a fire, the graphite expands and chars to resist fire penetration and spread, or to make high-performance gasket material for high-temperature use. After being made into graphite foil, the foil is machined and assembled into the bipolar plates in fuel cells. The foil is made into heat sinks for laptop computers which keeps them cool while saving weight, and is made into a foil laminate that can be used in valve packings or made into gaskets. Old-style packings are now a minor member of this grouping: Graphite intercalation compound Structure of CaC₆ Graphite forms intercalation compounds with some metals and small molecules. In these compounds, the host molecule or atom gets "sandwiched" between the graphite layers, resulting in a type of compound with variable stoichiometry. A prominent example of an intercalation compound is potassium graphite, denoted by the formula KC₈. Some graphite intercalation compounds are superconductors. Uses of synthetic graphite[edit] Invention of a process to produce synthetic graphite[edit] In , Charles Street of Le Carbone discovered a process for making artificial graphite. Another process to make synthetic graphite was invented accidentally by Edward Goodrich Acheson " In the mids, Acheson discovered that overheating carborundum silicon carbide or SiC produced almost pure graphite. This graphite was another major discovery for him, and it became extremely valuable and helpful as a lubricant. Scientific research[edit] Highly oriented pyrolytic graphite HOPG is the highest-quality synthetic form of graphite. It is used in scientific research, in particular, as a length standard for scanner calibration of scanning probe microscope. They are made from petroleum coke after it is mixed with coal tar pitch. They can vary in size up to 3. An increasing proportion of global steel is made using electric arc furnaces, and the electric arc furnace itself is becoming more efficient, making more steel per tonne of electrode. An estimate based on USGS data indicates that graphite electrode consumption was , tonnes in On a much smaller scale, synthetic graphite electrodes are used in electrical discharge machining EDM, commonly to make injection molds for plastics. The graphite scrap comes from pieces of unusable electrode material in the manufacturing stage or after use and lathe turnings, usually after crushing and sizing. Most synthetic graphite powder goes to carbon raising in steel competing with natural graphite, with some used in batteries and brake linings. Nuclear graphite Special grades of synthetic graphite, such as Gilsocarbon, [47] [48] also find use as a matrix and neutron moderator within nuclear reactors. Its low neutron cross-section also recommends it for use in proposed fusion reactors. Since they could not isolate the difficulty they were forced to use far more expensive heavy water moderators. Graphite used for nuclear reactors is often referred to as nuclear graphite. Other uses[edit] Graphite carbon fiber and carbon nanotubes are also used in carbon fiber reinforced plastics, and in heat-resistant composites such as reinforced carbon-carbon RCC. Commercial structures made from carbon fiber graphite composites include fishing rods, golf club shafts, bicycle frames, sports car body panels, the fuselage of the Boeing Dreamliner and pool cue

sticks and have been successfully employed in reinforced concrete , The mechanical properties of carbon fiber graphite-reinforced plastic composites and grey cast iron are strongly influenced by the role of graphite in these materials. Graphite has been used in at least three radar absorbent materials. It was mixed with rubber in Sumpf and Schornsteinfeger, which were used on U-boat snorkels to reduce their radar cross section. It was also used in tiles on early F Nighthawk stealth strike fighters. Graphite composites are used as absorber for high-energy particles e. Graphite mining, beneficiation, and milling[edit] Large graphite specimen. Naturalis Biodiversity Center Graphite is mined by both open pit and underground methods. Graphite usually needs beneficiation. This may be carried out by hand-picking the pieces of gangue rock and hand-screening the product or by crushing the rock and floating out the graphite. Beneficiation by flotation encounters the difficulty that graphite is very soft and "marks" coats the particles of gangue. This makes the "marked" gangue particles float off with the graphite, yielding impure concentrate. There are two ways of obtaining a commercial concentrate or product: In milling, the incoming graphite products and concentrates can be ground before being classified sized or screened , with the coarser flake size fractions below 8 mesh, 8â€™20 mesh, 20â€™50 mesh carefully preserved, and then the carbon contents are determined. Some standard blends can be prepared from the different fractions, each with a certain flake size distribution and carbon content. Custom blends can also be made for individual customers who want a certain flake size distribution and carbon content. If flake size is unimportant, the concentrate can be ground more freely. Typical end products include a fine powder for use as a slurry in oil drilling and coatings for foundry molds, carbon raiser in the steel industry Synthetic graphite powder and powdered petroleum coke can also be used as carbon raiser. Environmental impacts from graphite mills consist of air pollution including fine particulate exposure of workers and also soil contamination from powder spillages leading to heavy metal contamination of soil. Occupational safety[edit] People can be exposed to graphite in the workplace by breathing it in, skin contact, and eye contact. United States[edit] The Occupational Safety and Health Administration OSHA has set the legal limit permissible exposure limit for graphite exposure in the workplace as a time weighted average TWA of 15 million particles per cubic foot 1. A new electrode replaces the old one, but a sizeable piece of the old electrode remains.

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