The Physics of Fullerene-Based and Fullerene-Related Materials

Edited by

Wanda Andreoni

Physics and Chemistry of Materials with Low-Dimensional Structures

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Physics and Chemistry of Materials with Low-Dimensional Structures

VOLUME 23

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PREFACE BY THE EDITOR

The aim of the present book is to give an overview of the research of the past decade on materials either directly based on fullerenes (e.g. by doping) or whose discovery and concept were "born" from the work on fullerenes (e.g. carbon nanotubes). Such an overview is not just an intelligent collection and comparison of observations and of their interpretation but is often critical and clarifies open questions as well as interesting but not sufficiently explored aspects of these materials. As such, it should stimulate us to deepen our understanding of the physics and chemistry of these systems. In fact, the extent of our knowledge is still not satisfactory and quite uneven. On the one hand, we realize that in some cases even small details are known, and debates exist about academic issues. On the other hand, important questions of global and profound meaning such as the mechanisms that drive superconductivity in certain fullerides, those that are responsible for polymerization in others, or those that determine the remarkable transport properties of nanotubes still await an answer. This lack of knowledge is probably currently inhibiting the full exploitation of the properties of fullerenes and nanotubes.

I would suggest, therefore, that the reader not only absorb in a passive manner the information provided by this book, but that he or she go through these chapters with a critical mind. My hope is that its reading helps classify "the known" and "the unknown", single out key questions and relevant results, identify what is missing and, possibly, generate new ideas for the approach to these materials.

I warmly thank all the authors of this book.

Wanda Andreoni

PREFACE

Ever since the fantastic paper by Krätschmer, Lamb, Fostiropoulus and Huffman in 1990 showed us how to make viable quantities of C_{60}, research on fullerenes has gone from strength to strength. No less amazing has been the explosion of research into the related nanotubes which followed their discovery by Iijima. It is now almost impossible to take ourselves back to the era prior to 1990 when some even had difficulty accepting that the C_{60} molecule could form at all. It is even more difficult to remember the period prior to 1985 (the year in which C_{60} was discovered) when it was but a twinkle in the eye of a very small number of very imaginative individuals such as Osawa and Yoshida, Bochvar and Gal'pern as well as Davidson. There had also been a few prescient scientists, such as Chapman, who had tried to devise synthetic routes to C_{60}.

For those of us who have been closely involved with C_{60} from the early period it is even difficult accept that we have had the material in our hands for nearly ten years. However in this time it has revealed some quite fascinating behaviour. This compendium is a fine example of how far the fields of fullerene chemistry, physics and materials science have come in this period. The fact that the field is now becoming a mature one is very much a tribute to the wide range of interdisciplinary research that the charismatic molecule has catalysed. As the twenty-first century approaches we are beginning to see an almost seamless conflation of many areas of chemistry, physics and biology and the multitalented C_{60} molecule is a perfect medium for this exciting phenomenon. The set of articles published here encompasses a nice range of C_{60} research advances mainly across the chemistry-physics areas.

It is particularly nice to find that in the first article on the production of fullerenes, by Krätschmer who is one of the pioneers of the field, some fascinating astrophysical issues are discussed. This is a pertinent reminder that the field was originally born, partly serendipitously, during the course of two parallel, quite modest, fundamental astrophysical research projects.

Knupfer, Pichler, Golden and Fink have reviewed the exciting electronic properties of fullerenes from the experimental viewpoint and Andreoni and Giannozzi have discussed them with the aid of Density Functional Theory. Many fascinating areas such as the chemistry of intercalation compounds and the related electronic behaviour are reviewed. If any molecule is likely to play a part in the coming molecular electronics revolution it is C_{60}. In fact it is hard to believe that it will not, in time, be a star performer in this excitingly promising area. Material science also may be on the verge of a revolution if the putative properties of "long, tall, thin" cousins of the fullerenes, the amazing nanotubes can be realised. With emotive phrases bandied around such as: 50-100 times stronger than steel at one sixth the weight; and conducts like a metal or semiconducts like silicon, these tiny tubes appear to be the holy grail of 21st Century materials science. Dresselhaus, Dresselhaus, Eklund and Rao have given a very detailed account of the present state-of-play in this important area. Louie has discussed the exciting new advances in related non-carbon structures. A new dimension is starting to open up as the electronic behaviour of the nanotubes and related boron and nitrogen doped systems is revealing interesting possibilities.

Prassides has discussed the formation of polymer and dimer phases created via cycloaddition between C_{60} cages in solid alkali metal doped fullerene and heterofullerene materials. The vibrational behavior of the C_{60} cages is a novel problem and it has opened up new dimensions in molecular dynamics. Kuzmany and Winter review fullerene cage dynamics in crystalline solids, dimeric systems and polymers as well as metal doped and endohedral systems.

Fullerene intercalation compounds are particularly interesting and their properties are discussed by Yildirim, Zhou and Fischer in three chapters focusing on a) on their production, characterisation and physical properties, b) the structure and superconductivity of the alkali metal fullerides, and c) other fullerides and intercalated nanotubes. The amazing discovery of superconducting behaviour in K_3C_{60} opened up a totally new perspective on the types of materials that can exhibit superconductivity.

Pressure studies on carbon have a long history and as time has gone on the reason for the complexity has become clear – the incredible diversity of carbon species in the gas and condensed phases. The fullerenes have added a fascinating new dimension to this research area and recent results are reviewed by Núñez-Regueiro, Marques and Hodeau.

Few new compounds have promised so much or seem to still have so far to go to fulfill that promise as do the fullerenes and nanotubes – some 15 years after their discovery. But then what can one say about a family that can, at one limit, be a molecule and at the other a refractory particle. C_{60} is a round molecule 1 nm in diameter whereas the onion-like concentric shell graphite particle can be massive with as many as 10^7 and more atoms. In between are the stick-like nanotubes that can be 1 nm in diameter and theoretically, at least, miles long. To create the fantastical "Space Elevator" (made famous in Arthur C. Clarke's "Fountains of Paradise") the nanotubes will need to be many thousands of miles long, collected into bundles of the order of a meter wide and they must contain some 10^{18} separate tubes. This looks like a bit of a "tall" order to me at this time when we have such poor control over making the nanotubes in microgram quantities and a very poor understanding of the growth mechanism. All in all, this well-rounded compendium is a welcome addition to an important field.

Sir Harold Kroto

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PRODUCTION OF FULLERENES

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1. Introduction

Carbon not only has enormous industrial importance on earth, it is also the most abundant condensable element in our milky way. Surprisingly, it was the latter feature which lead to the discovery of fullerenes. The key experiments were conducted in search of carbon molecules and solid particles which are supposed to be abundant in interstellar space. C_{60}, the most important fullerene was discovered when H.W. Kroto, R.F. Curl, R.E. Smalley and co-workers investigated the mass-spectra of laser-evaporated carbon-vapor, which was quenched by a helium atmosphere [1]. These researchers who in 1996 gained the Nobel-Price in Chemistry for their work, initially intended to study how large carbon chain molecules form in interstellar space. In order to explain the ubiquitously occurring and strikingly strong interstellar UV absorption at 220 nm, Donald Huffman and I tried to produce interstellar-analogue graphitic particles in the laboratory. To our surprise, we obtained large amounts of C_{60} along with graphitic soot particles [2]. With this synthesis we opened the way for large scale fullerene research, which spread out almost explosively into chemistry, physics, and material sciences. Up to now it is unclear to what extent fullerenes have any impact in the research of interstellar matter. Maybe, in this case we missed the goal, and fullerenes or related cage structures play no or only a marginal role in the interstellar medium. In any case, for most interstellar particle or molecule absorptions, carbon in some form must be responsible. It thus may be worthwhile to give a short overview of the relevant astronomical data, partly in the hope that researchers in other fields may come up with new ideas in identifying some of these mysterious interstellar features.

2. Interstellar Absorption and Emission Features

Very roughly the interstellar medium may be divided into two domains, namely the ex-

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tended diffuse medium with densities of around one H-atom cm^{-3} or less, and the dense cloud medium in which the density may be much higher. The diffuse medium can be - and has been - extensively studied by spectroscopy ranging from the UV to the IR. There, most of the enigmatic absorptions and emissions occur which, so far, could not be satisfactorily explained. Fig. 1 shows the average extinction spectrum of the diffuse interstellar medium, measured in the vicinity of our solar system and along the especially dusty galactic plane. The spectrum refers to a column-length of one kpc (about 10^{21} cm). Extinction is the loss of light intensity out of the beam, i.e. the sum of absorption and scattering. For particles much smaller than the considered wavelength, extinction essentially equals absorption. In going from the UV longwards in wavelength, the interstellar extinction spectrum exhibits an intense "220 nm" hump, which turns out to be mainly absorption. The hump was discovered in the early 1960's during rocket-borne observations of stellar UV spectra [3]. Already in these early days Stecher and Donn suggested that small graphitic particles produce the 220 nm absorption. This hypothesis still remains the most likely one, even though laboratory spectroscopy performed on graphitic grains so far yielded only limited support for this identification.

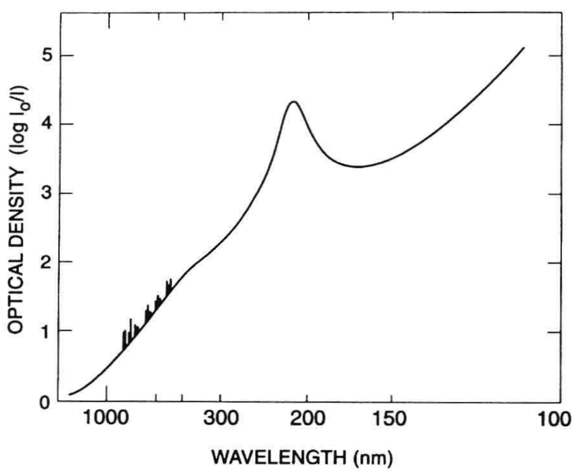

Figure 1. The average extinction spectrum of the interstellar medium in our solar neighborhood. Notice the intense absorption in the vicinity of 220 nm, which probably comes from graphitic nano-particles. The diffuse interstellar bands are indicated in the left part of the spectrum.

Furthermore, there are the mysterious "diffuse interstellar bands" (DIBs), extending from about 440 nm up to the red or even NIR part of the spectrum [4,5]. These bands are called "diffuse" since they are much broader (up to a few nm) than those of common interstellar atoms or molecules. On the other hand, these features are much narrower than the bands of most solid state materials. The most intense DIBs were already dis-