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New Trends in Solid State Physics

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特別寄稿
Guest
Forum

New Trends in Solid State Physics

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<Experience>
1968: Assistant professor at the Humboldt Univ.
1970: Professor at the Humboldt Univ.
1978-1990:
Prodean of the Faculty of Science at the Humboldt Univ.
1991-1992:
Visiting professor at the Univ. Paris.
1992-:
Visiting professor at the Ritsumeikan Univ.

<Research Activities>
1960-1964:
Magnetism,
1963-1980:
Fermi surfaces of metals,
Superconductivity,
Semiconductor and metal physics,
Crystal growth in space,
1976-:
Two dimensional electron systems,
Quantum Hall Effect,
1987-:
High temperature superconductivity and scanning tunneling microscopy.

1. Introduction: Basic Results in Physics

Solid state physics dates back to the end of the last century, when Paul Drude developed a theory of the electrical conductivity in metals, based on the experimental results. At the beginning of this century Max von Laue, W. Friedrich and E.P. Knipping opened the way for the determination of the structure of solids by their discovery of the x-ray diffraction in crystals1), which was completed by W.H. and W.L. Bragg with the analysis of crystal structures by means of x-rays2) and the x-ray element analysis by G.Y. Mosley.

Soon after the development of quantum mechanics, a macroscopic theory of the electronic properties of solids was presented by A. Sommerfeld and H. Bethe in the *Handbuch der Physik XXIV/2*(1928).

The discovery of the transistor by W. Shockley, J. Bardeen and W. H.Brittain3) in 1947 was a revolution in science and gave rise to the development of semiconductor technology, which governs the communication and computer electronics of modern life.

The discovery of the quantum tunneling effect in semiconductors, metals and superconductors, for which Leo Esaki, J. Giaver and B.D. Josephson won the Nobel Prize in 1973, had a great impact for the development of solid state devices, especially detectors.

After this successful application of solid state physics to the development of technology and industry, which was furthered by the introduction of solid state lasers, and semiconductor diode lasers, it was generally accepted that most of the development in solid state physics was completed and that in the second half of our century new fundamental results should come from other fields of physics like elementary particle or astro physics. Therefore it was surprising and fascinating that in the last decade new fundamental results and discoveries with great technological applications emerges once again from the field of solid state physics such as the discovery of the Quantum Hall Effect(QHE), the High Temperature Superconductivity(HTSC), the Scanning Tunneling Microscope(STM) and the superconductivity of metal doped Buckminster fullerenes.

The discovery of the Quantum Hall Effect 1980 by Klaus von Klitzing4) was a fundamental result which determined with extremely high accuracy the Sommerfeld fine structure constant and gave us a basic unit for the definition of the electrical resistance in Ohm.

In 1982 Gerd Binnig and Heinrich Rohrer invented a new image technique which, in contrast to conventional microscopes, made use of the tunneling current between the flat atomic conducting surface of a solid and an extremely fine metallic tip. This Scanning Tunneling Microscopy can image individual surface atoms with unprecedented resolution5). **Figure 1** shows STM images of Buckminster fullerenes of a (111)7×7 silicon surface. In addition to the fullerenes, silicon crystal planes (in **Fig.1(a)**) and single silicon atoms (in **Fig.1(b)**) are clear resolved[6]. Some time later, in 1986, Binnig developed together with G.F.Quante and C.H.Gerber the concept of using forces to image surfaces[7], such as the van der Waals force between a tip and a surface which was extended to magnetic and electrostatic interactions between magnetic or electric surface structures and a corresponding tip. These microscopes are named Atomic Force Microscope(AFM), Magnetic Force Microscope(MFM) etc..

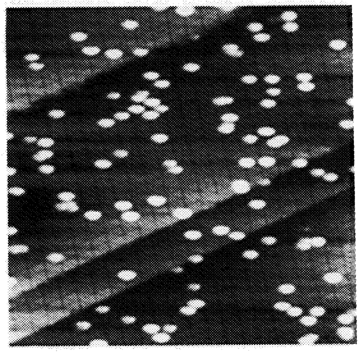

Fig.1(a) STM image of Si(111)7X7 surface covered with C_{60} molecules of 0.03 monolayer.

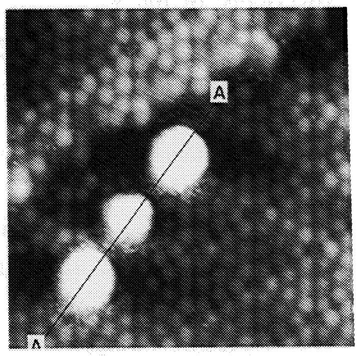

Fig.1(b) Three C_{60} molecules on the Si surface(larger magnification).
Si atoms are clearly resolved in the background also.

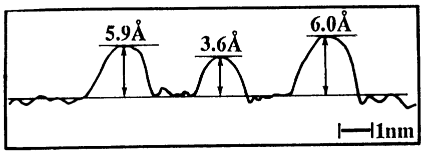

Fig.1(c) The hight of the C_{60} molecules is between 3.6 and 6Å [6]

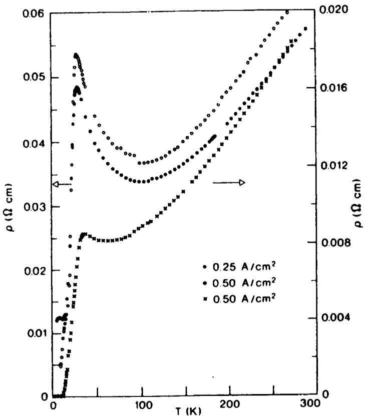

Fig.2
Resistivity of the HTSC La_2CuO_4 doped by Ba in dependence of the temperature.
The lower curve shows that at about 30K the resistivity goes to zero[8].

Moreover, the discovery in 1986 of High Temperature Superconductivity in ternary perovskite-related cupperates by Karl A. Müller and Johan G. Bednorz initiated a world wide boom, in the search for new "Zürich Oxides", unique in the history of science. Since 1972, the upper temperature limit for superconductivity was at 23K for an AlGe compound. In contrast to other scientists which working with metals and metallic alloys, Müller and Bednorz were searching for new superconductors in metallic oxides unusual for superconductivity at this time.

The first High Temperature Superconductor $La_{1.8}Ba_{0.2}CuO_4$ has a critical temperature of about 35K[8](**Fig.2**). Only one year later the temperature limit for superconductivity was at 93K, for the compound $YBa_2Cu_3O_7$, an amazing 15K over the boiling temperature of nitrogen[9].

A new technology was born. Although a low temperature superconductivity technology has existed since the sixties, this new oxide technology represents a great challenge.

In September of last year Science informed that new Hg based oxide reaches a critical temperature of 153K (or −123℃) under high hydrostatic pressure[10] (**Fig.3**). This result gives hope for a further increase in the limit temperature.

In addition to increasing activities in the field of High Temperature Superconductivity, a new material, the Buckminster fullerenes, is giving rise to hot discussion in the scientific community. In September 1990 W.Krätschmer, L.D. Lamb, K. Fostiropoulus and D.R. Huffman11) first published their results concerning the manufacture of macroscopic amounts of the carbon cluster C_{60}. This beautiful, soccer-ball-like carbon molecule was found in 1985 by H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl and R.E. Smalley12) in laser evaporation experiments. In solid form it condenses into a fcc cubic crystal structure and when doped by alkali metals, becomes a new High Temperature Superconductor. In addition to C_{60}, there presently exist a large family of fullerenes C_n, where n is an even number. These fullerenes give rise to a new view on the carbon based molecules and solids.

For the Quantum Hall Effect, the Scanning Tunneling Microscope and the High Temperature Superconductivity, the Nobel Prize was awarded in 1985, 1986 and 1987, correspondingly.

In this paper a short report is given about the Quantum Hall Effect and the fullerenes.

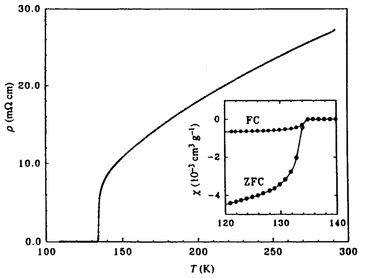

Fig.3
The resistivity ρ and DC magnetic susceptibility of $HgBa_2Ca_2Cu_3O_8$ under normal pressure in dependence of the temperature.
The transition temperature to superconducting state is about 135K10).

2. The Quantum Hall Effect

With the development of semiconductor technology basic research on microelectronic structures increased rapidly. Of special interest was the investigation of the Hall effect on the field effect transistor, the most frequently used structure in the integrated circuits.

The idea of the field effect transistor(FET) dates back to Charles F. Mott at the beginning of our century. William Shockley was the first person who tried to use silicon films for this effect. As a devise the field effect transistor was invented in 1960 and today it is the basic element for computer memories and amplifying semiconductor devices.

The Hall effect enables us to measure the sign and the absolute concentration of the charge carrier. **Figure 4** shows the Hall arrangement for a three-dimensional sample. The resistance of the sample is **R=U/I** and the Hall resistance across the sample is

$$\mathbf{R_H} = \frac{\mathbf{U_H}}{\mathbf{I}} = \frac{\mathbf{B}}{\mathbf{end}} \qquad \cdots\cdots\cdots(1)$$

(**e**: electron charge, **n**: carrier concentration per cm^{-3}, **d**: sample thickness).

Field effect transistors of Si (and $GaAs/Ga_{1-x}Al_xAs$ heterostructures) operate basically on the conductivity of a very thin surface layer of electrons ($d \cong 100Å$) which appears under the influence of a positive electrical field applied at the gate of

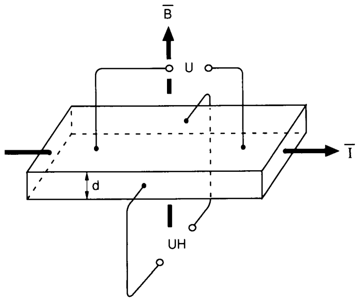

Fig.4
The Hall effect measurement arrangement.
The magnetic field B is perpendicular to the current I and the Lorentz force F~I × B forces the current carrier from the linear path aside. This drift motion is compensated by the Hall Voltage U_H, which determines the Hall resistance by(1). The voltage U gives the sample resistance.

the Metal Oxide Semiconductor FET (MOSFET) and behaves quasi two dimensionally (**Fig.5**). Therefore the field effect transistor is the primary tool for studying two-dimensional electron systems. The motion of the electrons perpendicular to the layer is not possible, but in the plane the motion is free.

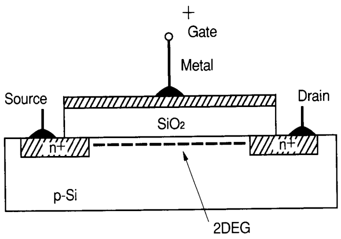

Fig.5
A scheme of a field effect transistor. The positive gate attracts electrons to the Si surface under SiO_2 and an inversion layer with the 2-dimensional electron gas appears.

If at low temperatures a strong magnetic field perpendicular to the surface restricts the motion of the electrons in the plane on orbits around the magnetic field lines, the electrons are localized on "two dimensional magnetic quantum levels".

The Hall effect of such an quantized electron system does not show the typical linear magnetic field dependence of a bulk sample but series of flat plateaus (**Fig.6**). The magnetic quantum levels are insulated from each other. Only if the electrons move with increasing magnetic field from a higher to a lower level does the Hall resistance increase. But for large magnetic field ranges the number of electrons in the levels does not change, the Hall resistance shows plateaus and the resistance along the sample in the plateaus area is zero.

Finally, at very high magnetic fields only one magnetic quantum level is filled. The Hall resistance in these plateaus is

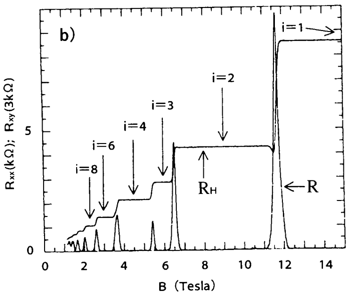

Fig.6
Magnetic field dependence of the Hall Resistance ($R_{xy} = R_H$) and the resistance(R_{xx}=R) along the sample at T = 50mK.
The integer i = 1,2,3,4,5,6 denotes the Hall Plateau resistance given by (2).
The samples is an GaAs/$Ga_{1-x}Al_xAs$ heterojunction[13].

$$R_H = \frac{U_H}{I} = \frac{1}{i}\frac{h}{e^2}, \quad \frac{h}{e^2} = 25812.8025\,\Omega \qquad \cdots\cdots\cdots(2)$$

(**i**=1,2,3, ··· numbers of the plateaus).

It has an extremely high accuracy and today it can be measured with an un certainty of 10^{-8}. This value is only determined by the two fundamental constants, the Planck constant h and the electron charge e and is independent of any material parameter of the semiconductor and of its geometry.

The Sommerfeld fine structure constant (a magic number in quantum physics) is

$$\alpha = \frac{\mu c}{2}\frac{e^2}{h} = \frac{1}{137}, \qquad \cdots\cdots\cdots(3)$$

where μ is the magnetic permeability and **c** the speed of light, both given by definition. Therefore the measurement of U_H(=**h/e²**) is a direct measurement of α . The fine structure constant determines **H** and fundamental interactions of physics such as the absorption and emission of photons by electrons or the inner structure of the atoms.

As of the first of January 1990, the Quantum Hall Effect represents the physical unit Ohm. In 1985 in Japan the ETL used the value 25812. 8025 $\pm 0.13\,\Omega_{ETL}$ of a Si-MOSFET in a magnetic field of 15 Tesla at 1.3K as a resistance unit.

Soon after the discovery of what is now called the integrated Quantum Hall Effect Tsui et al.[14] found that in very strong magnetic fields, if the electrons are only in one magnetic quantum level, new Hall plateaus appear with broken quantum numbers $i=p/q(p=1,2,3,\cdots;q=3,5,7,\cdots)$(**Fig.7**).
This kind of Quantum Hall Effect is called the fractional Quantum Hall Effect, even now not completely understood.

However the Quantum Hall Effect exists not only in the two-dimensional electron gas on Si surfaces and GaAs/$Ga_{1-x}Al_xAs$ heterostructures. Together with my co-workers I observed the integral Quantum Hall Effect in the two-dimensional electron gas at grain boundaries of InSb[15] and of $Hg_{1-x}Cd_xTe$[16].

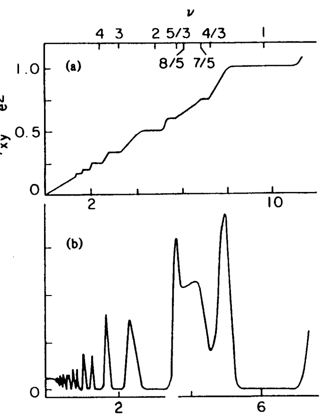

Fig.7
(a) Hall resistivity $\rho_{xy}(\sim R_H)$ and the (b) sample resistivity along a GaAs/ $Ga_{1-x}Al_xAs$ heterostructure at about 120mK.
The value ν indicates integer 1,2,3,4 and fractional values 4/3, 5/3 and 7/5, 8/5 [17].

3. The Fullerenes

W.Krätschmer et al.[11] were able to produce C_{60} molecules in abundant amounts. They collected C_{60} molecules from carbon soot produced in an electric erosion of carbon electrodes in a few hundred Torr helium atmosphere and purified them by liquid chromograph.

The fullerene C_{60} is a high symmetrical molecule with 12 regular pentagon and 20 regular hexagon faces. The carbon molecules undergo sp^2 and sp^3 hybridization resulting in two different bonds. One in pentagons with a length of 1.45Å and the other which is shared by two hexagons with the length of 1.40Å . The diameter of the cage is 7.1A(**Fig.8**).

As soon as C_{60} powder became available in macroscopic amounts small hexagonal crystals were grown from a benzene solution[18]. Investigations of C_{60} crystals and C_{60} thin films were then possible. Different crystal structures were observed by evaporating the solvent of the soot extract. Some crystals have a hexagonal shape with a hcp structure, others are cubic or whisker like with a fcc lattice. In the fcc lattice the C_{60} molecules rotate freely around their lattice points and at a relatively low temperature of about 250K a phase transition takes place from the fcc to a simple cubic lattice in which the cluster jumps between symmetric-equivalent orientations. In the fcc lattice the spacing between the centers is 10.04Å and the density is about 1.7g/cm^3. Pure fcc crystals are nonconductors and there is a clear correspondence between the energy levels of the C_{60} clusters and the energy bands of the fcc crystals. The band gap is 1.5eV.

Due to the internal network in the fullerenes the molecules lacks perfect spherical symmetry. But the steady rotation of the molecules modify this handicap and smooths out any sharp energy edges. The effective masses are 1.5 m_e in the conduction band and 1.5 m_e and 3.4 m_e in the valence band and the static dielectric constant is 18 ± 4 [19].

Soon after the development of the famous production method of Krätschmer et al., Arthur F.Hebard et al.[20] announced that potassium doped C_{60} has a

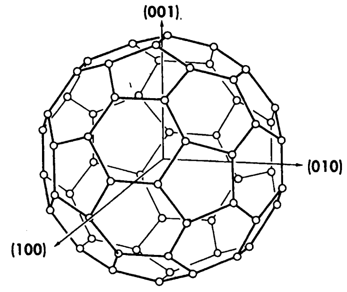

Fig.8(a)
C_{60} molecule placed in a fcc lattice. Each crystal axis crosses a double bound shared by two hexagons[19].

Fig.8(b)
STM image of a C_{60} molecule on the Si(111)7X7 surface shows the internal structure of the molecule[6].

superconducting transition temperature of 18K. In a high vacuum thin films of C_{60} are exposed to potassium vapour. An electrical conductivity appears and rises by several orders of magnitude in dependence of the increasing potassium concentration up to 3 alkali metal atoms per C_{60} molecule(e.g. K_3C_{60}). However, further doping decreases the conductivity and at 6 Potassium atoms per C_{60} molecule the conductivity disappears. The 3 alkali metal atoms are located in the octahedral and tetrahedral interstitials and the crystal is transformed from a van der Waals bonded lattice of C_{60} molecules into a ionic like bonded metal. Doping thin films of C_{60} by other alkali metals increase the critical temperature to 29K for Rb_3 C_{60} and up to 33K for Rb_2ScC_{60}[21]. Beside C_{60} there exist C_{70} and a whole family of fullerense C_n, where n is an even number, smaller or larger than 60. In every cluster the 12 pentagon faces remain.

The hollow spherical cage of C_{60} makes it possible to encapsulate atoms inside the molecule. Thus a new fullerene C_{82} is stabilized by lanthnum or yttrium atoms trapped inside the cage. These modified fullerenes, denoted as La@C82 or Y@C82, have been synthesized[22].

In electron macroscopic pictures carbon spheres each trapped within another and ordered like the layers of an onion are observed[23] and carbon nanotubes with different structures are found[24].

All these new carbon macro molecules and new carbon crystals enrich the world of carbon and the new solids should prove to be as interesting as the well known diamond and graphite.

4. Conclusion : Science and Technology

The existence of a new physical object with amazing new properties like the two-dimensional electron gas found in the metal oxide field effect transistor is an example of the enhancement of physics by technology.The Quantum Hall Effect shows all these two-dimensional properties in a comprehensive form. The high level of technology of the present days will increasing become the basis for new scientific discoveries.

The discovery of the High Temperature Superconductivity shows an alternative development route. It is the result of an intense,specific search for superconductors with high critical temperatures. Since the end of the seventies,there has existed an electronic and electrical power technology based on the low temperature superconductors Nb, Sn and NbTi, Nb_3Sn, V_3Ga, respectively. But the liquid helium cooling technology is very expensive for many applications especially for the storage of large amounts of energy without loss in magnetic coils or for levitated trains.

Therefore wires and tapes which operate at liquid nitrogen temperatures will have a large potential market. Today tapes are developed which have current densities of 10^5 A/cm^2 at 77K 25). Thin film devices such as low resistance microwave resonators and antennas, high sensitive infrared detectors and simple Josephson magnetometers which operate at 77K are currently being produced26).

The discovery of High Temperature Superconductivity by Müller and Bednorz is a result of an intensive basic research by a good organized team with a high scientific level at IBM Zürich. In the same company laboratory and in the same atmosphere, Binnig and Rohrer have developed the novel imaging principle on & nanometer and subnanometer scale using the well known quantum mechanic tunneling effect for their new microscope.

After the invention of the STM and AFM further imaging techniques were introduced like magnetic and electrostatic microscopes. STM and AFM can work in a high vacuum, in air and in liquids. Electrochemical investigations and the study of biological objects and molecules in the natural environment are common.

These new instruments allow the manipulation of single atoms and will be used in future for the construction of artificial molecules and possible atomic scale devices.

The discovery of the high symmetrical C_{60} cluster was stimulated by interest in a basic research problem, the properties of interstellar matter. The optical density of interstellar dust shows at 220 nm a broad hump, which was attributed to small particles of graphite. The search for these particles in the laboratory led to the discovery of the fullerenes. But the astro physical problem itself remains unsolved. This discovery and the potential application possibilities of the fullerenes shows that even at the present time basic research produces new scientific results which can change technology. I am grateful to Prof. T.Sakurai of the Tohoku University for the provision of the originals of the figures 1 and 8.

Remarks and Literature

1) Two years after the discovery of the x-ray diffraction Max von Laue won the Nobel Prize 1914.
2) Novel prize winners of 1915.
3) Novel Prize winners of 1956.
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「固体物理の新しい流れ」

19世紀の末，ドルーデが金属中の電気伝導に関する理論を発展させたことに始まった近代固体物理は，X線による構造解析や量子理論を導入して，今世紀の前半には基礎理論がほぼでそろった．第二次大戦後間もなくショックレーらがトランジスタを開発し，半導体による技術革命を起こした．さらに，江崎らの量子トンネル効果の発見が，社会をコンピュータと通信が支配する情報化時代へと導いてきた．一方，最近10年間の基礎科学における新たな発見と開発，たとえば，量子ホール効果，高温超伝導体，走査型トンネル顕微鏡(STM, AFM)，炭素クラスター分子群C_{60}，C_{70}などのフラーレン・ファミリーの発見などにより，固体物理が再び脚光をあびている．

基本的な半導体デバイスである電界効果型トランジスタ(FET)は，電子の二次元的挙動を研究するのには格好の素材である．金属や半導体に見られるホール伝導度は，低温・強磁場の下では一定となり，このとき電場方向の抵抗がゼロになる(量子ホール効果)．今では，ホール伝導度は10^{-8}レベルの高い精度で実測されるようになっている．最近二次元電子系で，ホール伝導度の変化が$-e^2/h$の非整数倍(1/3, 2/3など)に量子化される現象(分数量子ホール効果)も報告されており，筆者らはInSbやHgCdTeのグレイン・バウンダリーで集積量子ホール効果の存在を確認した．

1985年にクロトウらにより発見されたサッカーボール状の炭素クラスター分子C_{60}(フラーレン)は，1990年にクレチェメルらがこれをグラファイトのアーク放電法で大量に得る方法を発明し，種々の高次フラーレン群の構造や特性の研究が精力的に行われている．とくに，アルカリ金属をC_{60}結晶の格子間イオンとしてインターカレションした超伝導体の出現，クラスター・ケージの中に3d金属イオンを閉込めた内包型フラーレンの合成や，さらに金属カーバイドをキャプセル化した玉葱型多層構造，直径1nm程度の竹筒状ナノチューブ構造解析など次々と新たな炭素クラスター分子の研究が広がっている．

高温超伝導体の発見は，従来とは異なり，酸化物セラミックスに的を絞った研究の結果である．IBMチューリッヒ研究所のミューラらが高温超伝導性を発見し，おなじ研究所のビニッヒとローラーが量子トンネル効果を使ったSTMを開発して，ミクロからナノメートルスケールの世界を開いた．一方，C_{60}クラスターは，生命のルーツを求めて宇宙の星間物質へのあくなき探求心が刺激となって発見された．これらの発見と潜在的な応用への可能性は，今日でも，科学の基礎研究が技術をも変えるような新たな科学的な成果を生みだすものであることを物語っているだろう．

(文責　編集部)