PROGRESS IN ELECTRON PROPERTIES OF SOLIDS

PHYSICS AND CHEMISTRY OF MATERIALS
WITH LOW-DIMENSIONAL STRUCTURES

VOLUME 10

PROGRESS IN ELECTRON PROPERTIES OF SOLIDS

Festschrift in honour of Franco Bassani

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Preface

This volume on the novelties in the electronic properties of solids appears in occasion of Franco Bassani sixtieth birthday, and is dedicated to honour a scientific activity which has contributed so much of the development of this very active area of research. It is remarkable that this book can cover so large a part of the current research on electronic properties of solids by contributions from Bassani's former students, collaborators at different stages of his scientific life, and physicists from all over the world who have been in close scientific relationship with him. A personal flavour therefore accompanies a number of the papers of this volume, which are both up-to-date reports on present research and original recollections of the early events of modern solid state physics.

The volume begins with a few contributions dealing with theoretical procedures for electronic energy levels, a primary step toward the interpretation of structural and optical properties of extended and confined systems. Other papers concern the interacting state of electrons with light (polaritons) and the effect of the coupling of electrons with lattice vibrations, with emphasis on the thermal behaviour of the electron levels and on such experimental procedures as piezospectroscopy. Electron-lattice interaction in external magnetic field and transport-related properties due to high light excitation are also considered. The impact of synchroton radiation on condensed matter spectroscopy is discussed in a topical contribution, and optical measurements are presented for extended and impurity levels.

Electronic collective properties are to be taken into account to improve or modify the results obtained by the more traditional single-particle description. Excitons, their interactions, also in the presence of lattice coupling, are covered in a few contributions. Also more specific correlation effects in the presence of magnetic fields, in Auger transitions, and as origin of order phenomena are discussed. Collective effects in the theory of glassy and disordered materials complete the survey of this topic of large theoretical and experimental impact.

Other papers are devoted to nonlinear spectroscopy, a field which has grown in the last years as a refined implementation to traditional spectroscopy. The topics presented in the following deal with magnetooptics, coherence effects and multiphoton spectroscopy.

High-T_c superconductivity has by now become a turning point in material research. Theoretical approaches toward the understanding of different classes of superconducting materials are presented together with experimental photoemission results.

Finally, the wide area of two-dimensional electronic systems is largely covered with contributions on the optical properties of surfaces and layered coatings. A few papers are then devoted to the theoretical and experimental analysis of electronic states in superlattices and quantum wells; new theoretical approaches and computational procedures are examined for dealing with electronic levels and electronic transitions in such systems. More specific experimental effects in quantum wells, and theory of core excitons in superlattices are also considered.

In conclusion, we are confident that such a rich and various range of contributions gathered in this volume should constitute an adequate survey of present research on the electronic properties of condensed matter, as well as an appropriate tribute to Franco Bassani scientific achievements in the field.

The Editors

TO FRANCO BASSANI

On the occasion of his sixtieth birthday, October 1989

On October 29, 1989 Professor Franco Bassani, eminent Italian Physicist, celebrates his sixtieth birthday. A small group of his friends and colleagues has decided to mark this occasion, by presenting to him a collection of actual scientific results, elaborated by those physicists all over the world, who owe so much to Bassani's outstanding teaching and research work. The present volume is the tangible result of this decision, and although a severe selection had to be made among the very numerous potential contributors, the editors feel confident that it is representative of Bassani's tremendous influence upon the development of modern solid state physics.

Franco Bassani is born on October 29, 1929 in Milano, the capital city of Lombardia, the most industrious and fertile part of northern Italy. He studies physics at the University of Pavia, where, in November 1952, he obtains his diploma with special mention (laurea con lode). His excellent performances as a student earn him a stipend of the Italian National Research Council, which allows him to carry out his first personal research project on defects in ionic crystals at the University of Milan.

In 1954 he leaves Italy to pursue the same subject for two more years in the research group of Frederick Seitz at the University of Illinois in Urbana, USA. This first expatriation is of considerable importance for Bassani's professional development, since with Seitz, Bardeen and others, Illinois University had become a world famous center for solid state research.

Following his nomination in 1956 he comes back to his native country, where he holds the position of 'professore incaricato' (assistant professor) first at the University of Palermo and then, from 1957 to 1959, at his Alma Mater, the University of Pavia. It is here that he begins to develop the keen interest in the electronic structure of semiconductors and insulators, which constitutes one of the landmarks of Bassani's scientific work.

The dynamic evolution of solid state theory, which he had encountered earlier in Urbana, brings him back to the United States in 1959 as research associate of the Argonne National Laboratory in Argonne, Illinois. He continues his work on the electronic states in solids and makes his decisive contributions to calculations of band structures both by the tight-binding approach and the method of orthogonal plane waves. In this context he proposes a new procedure for band calculations, which has since become known under the name of pseudo-potential method, and he contributes actively to its development. Today this method is a well established tool, used by theoreticians around the world, permitting not only band calculations but also the determination of the total energy of crystals.

Early 1964 Bassani reintegrates Italy after having been nominated full professor at the University of Messina. His arrival there marks the beginning of a most impressive carrier in the Italian University System. Thus, in 1966 he becomes professor for theoretical physics at the University of Pisa, only to move on to Rome University in 1969.

If Rome appears to many as the culmination of a brilliant carrier, it could not entirely satisfy Bassani. Indeed, toward the end of the 1970's life in Rome had become difficult

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for the quiet, reserved and somewhat conservative professor, who does not shout with the leftist herds of the students. He takes a leave of absence (1979/80) to the long familiar University of Illinois, devoting himself entirely to his research, which after his second homecoming from the United States also includes studies of the optical behaviour of nonmetallic solids. This second landmark in Bassani's work comprises the first detailed analysis of the optical properties of graphite and germanium and the theoretical interpretation of a welth of experimental data on non-linear spectroscopy.

Even more than his band calculations his optical work brings Bassani in contact with experimentalists and makes him one of the first European solid state theoreticians working close to experiment. Thus, he plays an important role in the design and the interpretation of experiments on the Frascati Synchrotron, whose direction he assumes, while working at the University of Rome.

During his leave of absence from Rome, he is nominated ordinary professor of solid state physics at the most prestigious of all Italian Universities, the Scuola Normale in Pisa, that has been founded in the early 19th century by Napoleon. Here in the Toscana, where so many cultural and historical monuments mix with a most enchanting countryside, the culturally-minded Bassani has finally found in 1980 the peace and restfulness that he treasures so highly and that represents the well deserved reward for an outstanding contribution to modern science.

Bassani's carrier is marked by many displacements inside and outside of Italy. In his peregrinations he was always accompanied by his wife Serenella, who surrounded him with the care and comfort of a loving life companion. It certainly was not always easy for her to cope with the problems arising from Franco's many moves from institute to institute, from country to country. These problems were amplified by the presence of two wonderful children, Clara and Marco, who had to be looked after. It seems adequate, therefore, to say that Serenella, by assuming the heavy responsibility for most practical aspects of every-day life of the Bassani family, has largely contributed to the professional success of her husband. If we owe a lot to Franco for his physics, we also owe a lot to Serenella for making it all possible!

Dear Franco,

We first met at the occasion of your brief visit in summer 1964 at the Zurich laboratories of RCA. I have visited you in all the Italian Universities at which you tought, and in doing so, I have learned to love your country and to appreciate your compatriots. I have helped to bring you and your bright students many a time to the Federal Institute of Technology in Lausanne. Each visit brought an enrichment for me and I would therefore like, at this occasion to express my deep gratitude to what you have done for me and for the Institution at which I teach. And, of course, I add my very best wishes for your 60th birthday and all your future undertakings.

E. Mooser

THEORY OF BANDS, BONDS, AND OPTICAL PROPERTIES OF SEMICONDUCTORS

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This paper reviews and comments on the major developments in the area of optical properties of semiconductors. The focus is on the interpretation of structure in optical spectra in terms of interband transitions. Franco Bassani contributed pioneering papers in this important field which, in turn, had a large influence on our present understanding of the electronic structure of semiconductors and of solids in general.

1. Introduction

Franco Bassani's expertise covers many subfields of condensed matter physics. His contributions to the theory of impurity states, excitons, energy band theory, optical properties, and a host of other areas are well-known and well-documented by his excellent text [1], his papers, and the creative and important research done by him and his students. In this review, I will concentrate on an area where Bassani's research helped to launch an important subfield of solid state physics.

2. The Early Days

Although quantum mechanics was developed in the 1920's and atomic and molecular spectra were unraveled in the following 20 years, a similar situation did not exist for solid state physics. Optical spectra of metals in the intraband regime had been explored by Drude before the development of quantum mechanics. In Drude's model we visualize the free electrons classically with a mean free path determined by the electron scattering caused by defects or phonons. However, the quantum mechanical picture of solids predicted energy bands. The sharp atomic levels were broadened into bands, and it was assumed that transitions between the broad bands would lead to broad structure in the optical spectra in addition to intraband Drude-like structure.

Although this general view was supported by experimental measurements, there still was structure to be interpreted. It was not sharp on the scale of atomic spectra, but features could be distinguished, and they clearly were caused by interband transitions. The focus for semiconductors was on the fundamental gap, but unfortunately, band structure calculations were not refined sufficiently to predict the sizes of fundamental gaps let alone the entire spectra associated with interband transitions.

This was the situation in the early 1960's, and these are the 'early days' for this

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subfield of solid state physics. From a more formal point of view, schemes [2,3] for calculating band structures had been suggested, and the groundwork had been done for proceeding from the OPW method [3] to a pseudopotential approach [4]. The time was ripe for theorists to use the fact that nearly free-electron-like models for metals seemed to give good energy bands when these models were tested. An important advance was the concept of using experimental measurements such as those done with optical probes to give the data for empirical band structures.

The idea is to set up the band structure problem in terms of a potential which could be determined with just a few parameters [5-8]. The parameters, in turn, could be evaluated by comparing theoretical output with experiment. A crucial paper which established the most fruitful path was by Brust, Bassani, and Phillips [7] in 1962. Franco Bassani was at the Argonne National Laboratories, Jim Phillips was at the University of Chicago, and David Brust was a graduate student (as was I) at that time working with Phillips. The scheme was to fit three Fourier coefficients of the *Ge* potential and to calculate the imaginary part of the frequency-dependent dielectric function $\epsilon_2(\omega)$.

Brust traveled back and forth between the University and Argonne and provided the link between Bassani and Phillips. I kept up with the progress but did not get involved until one afternoon when Brust brought back a page of scattered dots from Argonne. This page contained the first realistic interband dielectric function $\epsilon_2(\omega)$ for a solid, but it looked like the results of a dart game. While Brust and Phillips discussed possible improvements, I began doing a three-point averaging by hand, and there was the spectrum.

I hadn't met Franco Bassani during that period, but I was being tutored indirectly by him through Brust. I was in awe of the achievement and of Bassani who then moved on to important research in other fields.

3. Pseudopotentials

Let me now discuss this work from the point of view of the development of pseudopotential theory. The pseudopotential was invented by Fermi [9] in 1934 (Fig. 1) to explain shifts in spectral lines of alkalai vapor arising from foreign gases [10].

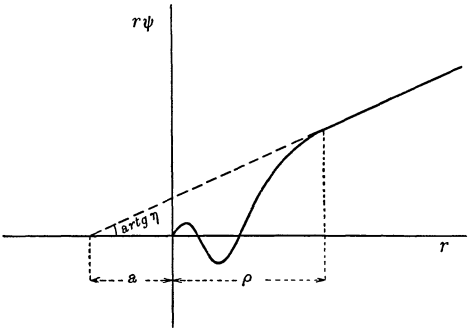

Figure 1. Fermi's approximation to the wavefunction to determine a pseudopotential for alkali atoms.

Hellmann [11] had also used a pseudopotential scheme to describe the energy levels of alkali atoms. The basic concept is to begin with atomic wavefunctions and then develop potentials which reproduce the outermost parts of the wavefunction.

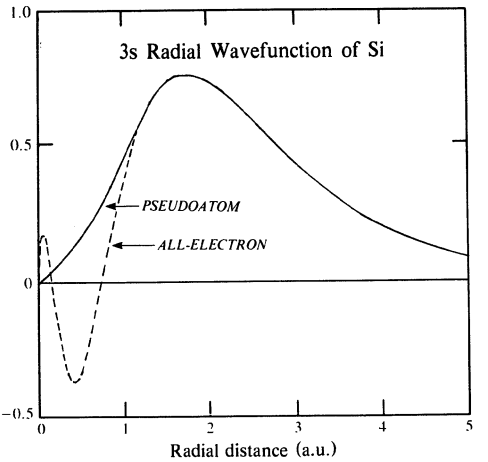

Figure 2. The 3*s* radial wavefunction for *Si* (dashed line) and the pseudowavefunction approximation (solid line).

The above approach is similar to modern schemes [12-17] (Fig. 2) where the pseudopotentials are primarily intended for solids. Since solid state effects are dominated by the outer positions of the electronic wavefunctions, weak potentials are constructed to reproduce this part and eliminate the nodes as shown in Fig. 2. The resulting potential behaves as an attractive Coulomb potential at large distances and is weak or repulsive in the core. This approach and the methods involved are well-documented in the literature, and they form the basis for the approximations made by Brust, Brassani, and Phillips [7].

The empirical approach usually called the Empirical Pseudopotential Method (EPM) assumes that the average potential $V(\mathbf{r})$ felt by an electron arising from electron-core and electron-electron interactions can be expressed in terms of a few Fourier coefficients of an atomic potential $V_a(\mathbf{G})$

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_a(\mathbf{G}) S(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \tag{1}$$

where the structure factor

$$S(\mathbf{G}) = \frac{1}{N_a} \sum_{\tau} e^{-i\mathbf{G}\vec{\tau}} \tag{2}$$

where N_a is the number of basis atoms, τ is the basis vector, and $\mathbf{G}$ is the reciprocal lattice vector.

The solution of the Schrödinger equation

$$\left[\frac{p^2}{2m} + V(\mathbf{r})\right] \psi_{n\mathbf{k}}(\mathbf{r}) = E_n(\mathbf{k}) \psi_{n\mathbf{k}}(\mathbf{r}) \tag{3}$$

gives the Bloch wavefunctions for each band n and state $\mathbf{k}$ and the energy eigenvalues. From these results, the $\epsilon_2(\omega)$ and the other optical constants can be computed [1,18].

Comparison between the calculated and observed spectra allowed the determination of the $V_a(\mathbf{G})$ in Eq. (1) by constraining the theoretical results to be consistent with experiment. Dozens of bands structures [18-20] were calculated, and when angular resolved photoemission was perfected, it was found that these band structures were in good

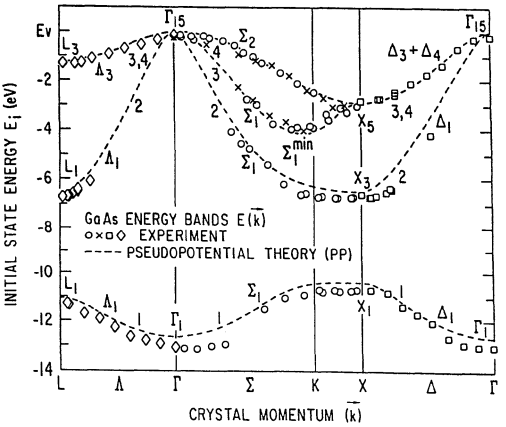

Figure 3. *GaAs* energy bands obtained from angular resolved photoemission experiment and from empirical pseudopotentials.

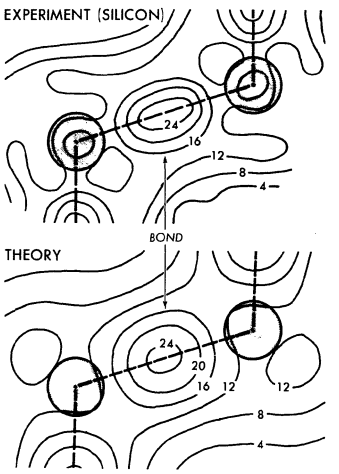

Figure 4. Contour plots of valence electron charge density for *Si* showing the comparison between experiment and theory.

agreement [18-20] with experiment [21] (Fig. 3). In fact, even the electronic charge density from the EPM calculations gave good agreement with experiment [18,22] (Fig. 4).

4. Some Extensions

Since the charge density was reliable and it is known that the principal change in electronic structure near a surface is the redistribution of electronic charge, schemes [23,24] were developed to separate the core part of the pseudopotential from the electron-electron part. Near a surface, the core contribution could be held fixed while the electron-electron contribution changes. This led to detailed calculations of electronic structure at surfaces [23,24] and interfaces [25].

Another important aspect of the charge density is its role in bonding. Phillips and Van Vechten [26] developed a theory relating the spectral features of semiconductors to their bonding. They were able to separate classes of structures and to develop an ionicity scale using dielectric information. By using pseudopotential results, it was possible to compute [27] the charge in the covalent bond and examine this property as a function of the Phillips-Van Vechten ionicity parameter. This scheme illustrated the role of the bond charge in stabilizing covalent structures. A recent scaling extension [28] of the above approach yields the bulk modulus for diamond and zincblende semiconductors.

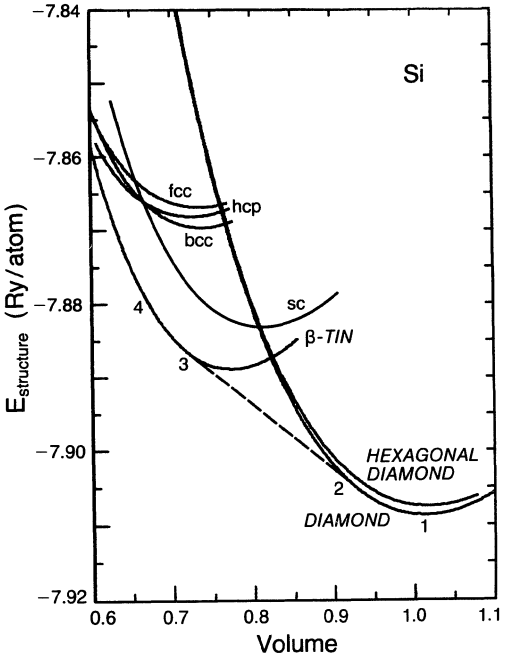

Figure 5. Total energy versus volume for *Si* in various crystal structures. The dashed line is a common tangent between the diamond and β-tin phases (see text).

The above approaches are semi-empirical, and they pointed the way for more first-principles calculations. The calculations were motivated by the consideration of structural properties of semiconductors. Since the approach for studying surfaces already separted the core from the valence contributions of the potential, a scheme was developed to calculate the total energy [29] of the solid for an assumed arrangement of cores while allowing the valence electrons to choose a minimum energy configuration. The calculation was based on a momentum representation [30] of the various energy terms.

A propotype result [31] is given in Fig. 5 where the total energy is plotted as a function of volume for several assumed structures of *Si*. These curves can be used to obtain the lattice constant (given by the volume at the minimum of the curve), the bulk modulus (curvature), and the transition pressure for a solid-solid structural transition. For example, the dashed line illustrates the paths for transforming *Si* from the diamond to the $\beta-Sn$ structure with reduced volume (increased pressure). At point 1, the solid is in the diamond structure, at 2 it begins to transform, at 3 the transformation is complete, and at 4 it is in the $\beta-Sn$ structure.

The total energy structural calculations gave results for structural reconstructions at

surfaces, phonon spectra, pressure-induced effects such as structural phase transitions, electron-phonon couplings, and was even responsible for successful predictions of superconductivity [32]. All of this was done from first principles. The calculations require only the atomic number, mass, and candidate structures.

5. The Situation Now

Despite the great success of the *ab initio* approach discussed above, three problems became evident. The first is the fact that the *ab initio* calculations are based on a density functional approach. Hence, the results are only appropriate for ground state properties. Excited states, band gaps, and quasiparticle properties are not treated correctly. For example, despite the fact that the method gives lattice constants and bulk moduli to an incredibly high degree of precision for *Si* and other semiconductors, the band gap is in error by 50%. Recent research [33] appears to have solved this problem by the introduction of quasiparticle self-energies and local field effects.

The second problem is the need for candidate structures to determine the crystal structure of a material. This is a form of input which theorists would like to avoid. Fortunately, good progress has been [34] made with simple systems, and extensions are being examined. By allowing atoms to move in a manner which reduces the total energy, it may be possible to find new structures and predict the existence of useful materials.

Finally, there is a need for better functionals for exchange and correlation. The cohesive energies of the solids studied, using density functional theory, are in relatively good agreement with experiment, but improvements are needed. Recent Monte Carlo techniques [35] show great promise.

At this point, the new developments appear to be capable of giving an *ab initio* theory which will give structural and other ground state properties and excited state properties. However, these approaches are complicated and have had application to only a limited number of crystals. It is hoped that the *ab initio* methods will be simplified and applied to a large number of solids, but at this point the largest number of accurate band structures are those determined with the empirical scheme which Franco Bassani helped to create almost 30 years ago.

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