Manuel Cardona

1934–2014

BIOGRAPHICAL *Memoirs*

A Biographical Memoir by
Marvin L. Cohen,
Francisco de la Cruz,
Lothar Ley, Miles V. Klein,
Michael Thewalt, and Peter Y. Yu

NATIONAL ACADEMY OF SCIENCES

MANUEL **CARDONA**

September 7, 1934–July 2, 2014

Elected to the NAS, 1987

Manuel Cardona

By Marvin L. Cohen,
Francisco de la Cruz,
Lothar Ley, Milev V. Klein,
Michael Thewalt ,
and Peter Y. Yu

Manuel Cardona Castro was born in Barcelona, Spain, and passed away unexpectedly in Stuttgart, Germany—while working at the Max Planck Institute (MPI) for Solid State Research—at the age of 79.

The Spanish Civil War had started four years after he was born, and his family suffered the consequences of that bloody conflict along with so many other Spaniards. The horror of war left a deep and lasting impression on Cardona and made him a champion for international peace. During his lifetime he was a citizen of three countries: Spain, of course; his adopted country of the United States, where he started his scientific research career and where all three of his children were born; and Germany, where he settled down, raised his family, and was finally laid to rest.

Cardona was a worldly individual. As a boy he traveled throughout Europe and learned a number of languages, which reflected one of his well-known skills. He was fluent in German, English, and French in addition to his native languages of Spanish and Catalan. He was a renaissance man whose interests extended beyond science to include literature, art, and music. He read widely and had a photographic memory. It was not uncommon for him to remember not only the year and volume but also the page numbers of his numerous publications.

But beyond his many other interests, his first and enduring love was physics, which Cardona began studying at the University of Barcelona, where he received a Licenciado en Ciencias Físicas (roughly equivalent to an M.S. degree in physics in the United States) in 1955; he then served for a year as an instructor in electronics at the University of Madrid. Cardona's scientific talent, recognized as a result of his work in college, in 1956 earned him the Spanish National Prize for Natural Sciences and also the Juan-March Foundation Fellowship to pursue graduate studies at Harvard University. Together with his Harvard thesis advisor William Paul, Cardona studied the dielectric properties of elemental semiconductors such as silicon and germanium, in particular the effect of high pressure on their dielectric constants and electronic energy bands. Cardona received his Ph.D. there in applied physics in 1959. Separately, the University of Madrid awarded him a D.Sc. degree in 1958—an important year for Cardona for another reason.

At a Valentine's Day party in Boston in 1958 Cardona met a German girl by the name of Inge Hecht. They were married one year later, also on Valentine's Day. From then on, Inge was always a major figure in his life. She was one of the reasons for his eventual decision to settle down in Germany, for example, and she was well loved by all the students and visiting scholars of the *Abteilung Cardona* (Cardona Group) at the MPI, including their spouses. It is not an exaggeration to claim that she was an integral part of the group and helped to make it feel like one big family.

Over the course of his career Cardona received a total of nine honorary degrees from universities around the world. In addition, his research in condensed matter physics was recognized through many awards, prizes, and other honors. He was a member of many learned societies, including the *Academia Europaea*, the U.S. National Academy of Sciences, the Royal Society of Canada, and the *Academia Nazionale dei Lincei* of Rome, which once counted Galileo Galilei among its members. The list of prizes he received included two from the American Physical Society (the Frank Isakson Prize and the John Wheatley Prize), the Blaise Pascal Medal of the European Academy of Sciences, the Sir Nevill Mott Medal and Prize of London's Institute of Physics, and the *Principe de Asturias* prize of Spain.

Cardona authored or coauthored more than 1,300 publications in international journals. From 1970 on he was one of eight most cited scientists in the world. As a result, he became interested in the statistical analysis of publications and citations (a science known as bibliometrics) as a hobby. Cardona authored or edited ten monographs on solid-state physics and coauthored a graduate textbook on semiconductors. He also served on the board of editors of seven journals, including *Solid State Communications*, for which was the editor-in-chief from 1992 to 2005.

Scientific career

From 1959 to 1961 Cardona was a member of the technical staff at the RCA Laboratories in Zürich, Switzerland. There he extended his doctoral research to the study of the optical properties of Group III–V semiconductors. In 1961 he moved to the RCA Laboratories in Princeton, New Jersey, where he continued to work on the optical properties of semiconductors, including the Group II–VI semiconductors. Based on his extensive measurements of the dielectric functions of semiconductors, he started observing similarities in their optical spectra. In particular, he realized that some peaks were split by spin-orbit coupling. It turned out that in a family of semiconductors with the same crystal structure, the reflectivity spectra often exhibit peaks due to electronic transitions occurring at similar regions in the Brillouin zone. Cardona introduced a notation to label these reflectivity peaks as E_0, E_1, E_2, etc., according to their origin in the reciprocal lattice space. This notation has since become the standard way to label optical transitions in semiconductors.

In 1964 Cardona joined the Department of Physics at Brown University in Providence, R.I., as an associate professor. He set up two different programs of experimental research. The first was a continuation of his past work on the optical spectra of semiconductors. The second line of research—superconductors—was a relatively new one for him, though he had started addressing it while at the RCA Laboratories in Princeton, New Jersey. There, Cardona and collaborators analyzed the nature of the electronic states in the core of the flux vortices in Type II superconductors. From microwave-absorption experiments they concluded that the energy dissipation associated with the vortex core was intrinsic to the superconducting state and should not be linked to thermally induced electronic excitations. As a result, they were among the first to suggest that the specific heat of Type II superconductors should exhibit a linear temperature-dependent contribution. This was subsequently confirmed experimentally. However, the major impact of Cardona's RCA work at Brown was in the area of modulation spectroscopy.

Before the 1960s, physicists interested in the optical properties of semiconductors typically measured either the absorption or the reflection spectra of their samples. Absorption spectra often exhibit sharp structures around the absorption edge of a semiconductor (especially at low temperatures). The onset of strong absorption occurs when the photon energy exceeds the band gap of the semiconductor. For photon energies much higher than the band gap, the absorption coefficient (α) often becomes larger than 10^5 cm^{-1}, so that the sample becomes opaque unless the sample thickness is smaller than a micrometer. Thus a major difficulty of measuring the transmittance of the sample is that the sample has to be thinned to submicron thickness once the photon energy is above the absorption edge. On the other hand, it is much easier to measure a sample's reflectance (R) when it is highly absorbing. The trade-off is that the reflectance spectra often exhibit broad features only.

In the early 1960s, several groups had started measuring the *change* in reflectance induced by external perturbations, such as those due to an applied electric field or stress. These derivative spectra of R can exhibit more and sharper structures. In particular, the change in R induced by a periodically varying electric field can be approximated by the third derivative of R with respect to the field. This method, known as electroreflectance, became a very powerful technique for studying inter-band electronic transitions and hence the electronic-band structure of semiconductors. Cardona and his group soon developed a technique to apply an external electric field to semiconductors using an electrolyte. The technique's advantage was that it could be applied to any semiconductor surface without requiring the growth of a Schottky barrier or a *pn*-junction on the semiconductor surface.

In addition to electric fields, Cardona's group extended the technique by applying other external perturbations, such as temperature and stress, to change the sample reflectance. This new kind of spectroscopy, based on modulating a sample's optical properties via external perturbations, became known as modulation spectroscopy. It later included the measurement of the wavelength derivative of the reflectance wherein only the wavelength of the incident light is modulated while the sample properties are unchanged. The extensive activity occurring in this field at that time was summarized by Cardona in 1969 in a monograph titled "Modulation Spectroscopy."

The interplay between theory and experiment has always been an important factor in the way physics advancements are made. Experimental results are obtained through carefully controlled measurements. When faced with overwhelming experimental evidence that exhibits a consistent and regular pattern, theorists will attempt to formulate physical "laws" to describe these results quantitatively; a correct theory will predict results that have not yet been observed. Such a theory will be "tested" by experimentalists by making further and often more precise measurements. As experiments and theory became more sophisticated, physicists began to specialize in one or the other.

Only rarely, an exceptional physicist will come along who can carry out both theoretical and experimental work at the highest levels. Enrico Fermi was one such physicist. And although Cardona made his most definitive contributions to experimental physics, his extensive efforts in explaining his many experimental results would also have easily qualified him as a theorist.

When modulation spectroscopy produced a wealth of information in the 1960s and '70s about the band structure of semiconductors—in the form of the energies and oscillator strengths of inter-band transition—experimental results overwhelmed the ability of theorists, at least for a time, to explain them. Eventually, theory caught up with experiment when theorists such as Marvin Cohen at the University of California at Berkeley developed the pseudopotential method of band-structure calculation. But before the method became popular, Cardona needed to provide his own theoretical framework for interpreting his group's semiconductor optical data. They wound up performing semi-empirical "**k.p**" band-structure calculations. Given that this was before the advent of high-speed computers, which would have made self-consistent and first-principle calculations possible and sufficiently accurate to explain and even predict experimental results quantitatively, the **k.p** technique provided a simple framework for understanding the relationship between the band gaps and band parameters—such as effective masses and g-factors of electrons in solids.

Cardona's approach to theory was often heuristic—based on physical insights rather than mathematical rigor—much to the appreciation of experimentalists and theorists alike. But after first-principle band-structure calculations based on density functional theory had become well established, Cardona and his collaborators readily embraced the technique and even extended it to include spin-orbit coupling, once they had discovered this phenomenon's effect on the phonon frequencies of semiconductors, such as PbTe, containing large-Z elements.

In the summer of 1965 Cardona visited the University of Buenos Aires under the auspices of the Ford Foundation. He started collaborations with several of the university's researchers, but these efforts were interrupted in 1966 when a military dictatorship took over the institution. Cardona described what then happened to his collaborators in some of his many email exchanges with his former student José Menéndez.[1] For example:

> *Perhaps you would be interested to learn that during my stay at Buenos Aires I collaborated with Ricardo Sussman. When the 'Night' happened,[2] he was in the People's Republic of China with a scholarship from the Chinese government. Clearly, he could not return to Argentina. His wife Silvia, then personal secretary of Dean Rolando Garcia, was beaten by the police batons. She is the one who phoned or telegraphed Ricardo asking*

---

[1] See article by J. Menéndez in *Manuel Cardona., Memories and Reminiscences.* Edited by Klaus Ensllin and Luis Vina . pp.87. 2016. Heidelberg: Springer.

[2] During the infamous "La Noche de los Bastones Largos" or "Night of the Long Batons" on July 1966 federal police stormed the University of Buenos Aires and arrested students and faculty who had taken over five departments in opposition to the military government's intervention with the universities.

> *him not to return. With my help and that of [David] Greenaway…,Ricardo found a temporary position with RCA in Switzerland.*

Following this trip, a steady stream of Argentinian graduate students and postdoctoral fellows came to Brown to work in Cardona's group. And throughout his career, he came to the aid of Argentinian physicists when they got into trouble with their military government. This "globalization" of his research group later expanded to include visitors from all over the world, and it continued even after he left Brown to become one of founding directors at the MPI in Stuttgart, Germany. For his work in promoting research in the Latin American countries—such as Argentina, Mexico, and Cuba—Cardona was awarded the John Wheatley Prize of the American Physical Society in 1997.

Before he left Brown, Cardona started to investigate the effect of stress on optical phonons in semiconductors by collaborating with Elias Burstein, who Cardona had met while serving as a visiting professor in spring 1963 at the University of Pennsylvania; Burstein had helped to build the physics department there into one of the leading centers in condensed matter physics. At the time of their first collaboration, no commercial equipment was available for performing Raman scattering to study vibrational modes (phonons) in solids. However, Burstein had a talented technician in his group who constructed a double spectrometer capable of discriminating the strong-excitation light from the weak and inelastically scattered light, which contained information on the phonons.

When double spectrometers became commercially available, Cardona put together a Raman scattering laboratory at Brown immediately. During the second collaboration with Burstein that soon followed, Cardona also worked with Burstein's student, Aaron Pinczuk, who came from Argentina. Like many other Argentinian physicists, Pinczuk was quickly attracted to Cardona.

The study of the properties of phonons eventually became one of Cardona's lifelong passions, and so were his friendships with Burstein and Pinczuk. Cardona considered Burstein to be his mentor. Among the many things he learned from Burstein was the love of the bolo tie!

One of the journals founded by Burstein was *Solid State Communications*, and when Burstein retired as its editor-in-chief, Cardona succeeded him. When Cardona retired from that post, he "passed the baton" on to Pinczuk.

Cardona taught a graduate-level introductory course on solid-state physics several times while at Brown. He was an enthusiastic, engaging, and approachable classroom teacher. Treating every student as his equal, he often worked in the lab along side with his students and postdoctoral researchers; and he was a hard worker, setting a high standard for his many collaborators, thereby motivating them. He mentored over 100 graduate students and postdoctoral fellows throughout his career.

In 1969, Cardona created the first graduate-level course devoted entirely to the optical properties of semiconductors. His approach to this subject was mainly empirical but grounded in theory. And just as with the **k.p** theory, physical insight and understanding were emphasized more than mathematical rigor. He did not have a chance to repeat this course, as a result of his departure from Brown, but one of his students, Peter Yu, later developed it into a graduate-level course on the physics of semiconductors at the University of California, Berkeley. Cardona and Yu coauthored a graduate-level textbook (1996) on the physics and material properties of semiconductors. This book proved to be very popular with students and researchers worldwide, and it was translated into three other languages (Japanese, Chinese, and Russian). Through this textbook, Cardona was able to educate many more generations of students in his special approach to understanding semiconductor physics.

During the 1969–1970 academic year, Cardona was awarded a John S. Guggenheim Memorial Foundation Fellowship, which allowed him to spend a year at Germany's Electron Synchrotron (known also as DESY) in Hamburg. This visit turned out to have two important impacts on his future career.

First, Cardona started pioneering experiments using the synchrotron radiation with photon energy in the vacuum ultra-violet (VUV) region to explore transitions from core levels to the conduction bands in solids. The operation of the synchrotron in those days was dominated by the high-energy physicists, for whom the radiation emitted by electrons when circulating inside the synchrotron was an undesirable byproduct. As a result, the stability of the synchrotron radiation was highly unpredictable, and not under the control of the condensed-matter physicists. Although these experimental conditions were difficult, the resultant optical spectra often could not be obtained with any other means.

Cardona demonstrated through a series of measurements that from such core-level transitions the conduction-band density-of-states (DOS) of solids could be determined directly, given that the core levels were so localized that they had negligible dispersion. As a result, their DOS were like delta-functions. These core-level transitions had clear advantage over the inter-band transitions measured in the visible reflectance, as the latter depended on the DOS of both the conduction and valence bands.

Second, through his synchrotron radiation experiments, Cardona became interested in other experiments using VUV and X-rays, such as photoemission experiments. While core-to-conduction-band transitions can determine the conduction-band DOS, X-ray photoemission can determine the valence-band DOS. When photoemission is observed with an electron analyzer capable of measuring the angular dependence of the photoelectrons in so-called angle-resolved photoelectron spectroscopy (or ARPES), the dispersion of the valence bands can be determined with high precision. Thus photoemission and modulation spectroscopy, applied in combination, can produce the most complete set of experimental results on the DOS of electronic bands, both occupied and empty, in a solid. Cardona's results became the basis of the most stringent test of any theoretical-band structure calculation of a solid.

In the 1970s photoemission was achieved with conventional X-ray sources, but with the availability of many synchrotron radiation facilities around the world, ARPES is typically done nowadays with synchrotron radiation. The availability of such powerful and accurate techniques to measure the electronic-band structures in solids has thus become the driving force for the rapid development of theoretical band-structure calculation techniques—from empirical to self-consistent and first-principle—as mentioned earlier.

While in Germany on his Guggenheim Fellowship, Cardona was recruited by the Max Planck Society to become one of the founding directors of the newly created Max Planck Institute for Solid State Research located at Stuttgart. Thus in 1971 he left Brown and moved his research group to Stuttgart. Cardona remained a director of the MPI until his retirement in 1999, but he remained actively involved in research there until the day he died. Because he had devoted so many of his active and productive years to the institute and had loved it so dearly, his burial in a small nearby cemetery, within walking distance, was indeed fitting.

When Cardona first arrived in Stuttgart, the MPI occupied an old building in downtown Stuttgart near the railway station. A brand-new building for the institute was being constructed outside the city, near the University of Stuttgart, but it would not be ready until 1975. In spite of the less-than-ideal and cramped building, Cardona wasted no time in restarting his research programs. He immediately set up a scattering system in which the excitation laser sources were tunable.

This kind of inelastic light-scattering technique became known as resonant Raman scattering (or RRS). It is really a “double” spectroscopic technique. In conventional light scattering, a fixed-frequency laser is used as the excitation light source while variations in the scattered light’s intensity—constituting the “Raman spectrum”—are measured as a function of the difference in frequency between the incident and scattered photons. The creation or annihilation of elementary excitations (such as phonons) is indicated by resonances in the Raman spectra. Also in conventional Raman scattering, the scattering medium is usually transparent to the incident photon in order to maximize the scattering volume.

In RRS, by varying the frequency of the incident excitation light sources as well, one can measure the variation in the scattering cross-section of a particular elementary excitation as a function of the incident photon frequency. The resultant Raman excitation spectrum (known as the *resonant* Raman spectrum) exhibits structures such as maxima or minima when the incident photon is absorbed by the medium to produce inter-band transitions. Thus RRS can probe the excitation of electrons by the incident photon, as in absorption and reflection spectroscopies, but RRS has the additional capability of capturing the interactions between photo-excited electrons and elementary excitations in a medium.

Cardona immediately took advantage of this technique to investigate electron-phonon interactions in semiconductors. He proposed that the technique could be considered a kind of “modulation” spectroscopy in the sense that the electrons are modulated by atomic vibrations. The resultant variation of the scattering cross-section with incident light frequency is related to how the dielectric functions are modulated by electron-phonon interaction. This approximate approach greatly simplifies the interpretation of the resonant Raman spectra and is valid when the phonon frequency is small compared to the damping of the electronic-excited states.

Light-scattering experiments remained a lifelong pursuit for Cardona. His many contributions to the field included the explanation of Fano-type interferences between Raman scattering due to electronic excitation of free carriers in doped semiconductors with phonon excitations; the anomalous temperature dependence of the optical phonon Raman line shape in the copper halides; electron-phonon interaction in the high T_c superconductors; effects of isotopic impurities on phonon modes; and, most recently, the application of inelastic X-ray scattering to determine phonon dispersion curves. (More detailed discussions of some of these topics are presented below.) Cardona also created and coedited *Light Scattering in Solids,*[3] a nine-volume series of monographs published by Springer between 1983 and 2007—which documented the progress in this field for over two decades.

In addition to expanding his MPI research into the vibrational properties of solids, Cardona took advantage of his new position to start extensive experiments in photoelectron spectroscopy and synchrotron radiation. His exposure to the unique properties of synchrotron radiation at DESY convinced him of the importance of dedicated synchrotron radiation (SR) facilities as a unique tool for the study of condensed matters. He recruited Lothar Ley, who was then a postdoctoral fellow at the University of California, Berkeley, to help him start a new MPI group dedicated to electron spectroscopy. His impact on synchrotron radiation research, in Germany and subsequently the rest of Europe, was enhanced by his 1975–1978 appointment to DESY's Scientific Counsel (*Wissenschaftlicher Beirat*), which he chaired from 1976 to 1977.

An important decision of that committee, which shaped the future of SR in Germany, was to recommend the construction of two dedicated SR sources: one storage ring with energy of 0.7 GeV to cover the ultraviolet part of the spectrum; and a 3 GeV machine for the X-ray regime. In the end, a 0.7 GeV storage ring was built in Berlin and started operation in 1982. Cardona first established his own photoemission setup, called Flipper II, at a dedicated synchrotron radiation laboratory at DESY. But after the 0.7 GEV storage ring in Berlin (known as BESSY) began functioning, Cardona got involved in the installation of a new kind of photoemission spectrometer, known as the Toroidal Analyzer Spectrometer, in collaboration with a group of scientists from the La Trobe University of Melbourne, Australia. Because the new design of this analyzer allowed the photo-electron spectrum to be measured over a full 180° arc, it was ideally suited for mapping with ARPES the dispersion of valence bands of solids. This spectrometer and its upgraded successors, installed at the next-generation storage ring BESSY II, were extremely productive; they served until 2012, well after Cardona's official retirement.

After moving to Stuttgart, Cardona temporarily stopped his work on superconductivity, but in 1986, when Georg Bednorz and K. Alex Müller of the IBM Research Laboratory in Zürich, Switzerland, discovered superconductivity in a new family of cuprate superconductors with transition temperature (T_c) above 40°K, this breakthrough renewed his

---

[3] *Light Scattering in Solids* is a nine-volume series in Topics in Applied Physics co-edited by M. Cardona and published by Springer between 1983 and 2007.

interest in that field. Not only was this discovery reproduced around the world, but the family of cuprate superconductors grew rapidly, with T_c pushed up to above 160°K; thus the family became known as the high-T_c superconductors (HTS).

A major research effort began immediately to explain the mechanism behind the high T_c in these materials, as the conventional theory proposed by Bardeen, Cooper, and Shrieffer ("the BCS theory") failed to do so. Because the electron-phonon interaction was central to the BCS theory, naturally there was great interest in the phonon properties of the cuprates; for their part, Cardona and his group applied their expertise in Raman scattering to investigate the phonons in the HTS. Cardona in particular attacked the problem with his usual vigor, and between 1987 and 2003 he authored or coauthored more than 150 papers on the subject. The Cardona team discovered anomalies in the properties of the Raman- and infrared-active phonons at $T_{c,}$ and many believed at the time that such anomalies were relevant to understanding the basic mechanism of superconductivity in these materials.

Cardona et al. also studied the role of various atoms in the lattice dynamics of one of the most commonly studied HTS—yttrium barium copper oxide (YBCO)—by measuring samples prepared with isotopically pure ^{16}O and ^{18}O. In this way, they demonstrated the near-absence of an oxygen-isotope effect on the superconductivity of these materials, in contrast to the presence of such an effect in conventional superconductors. In the family of HTS containing mercury—$HgBa_2Ca_3Cu_4O_{10+\Delta}$ (usually abbreviated Hg1234), which has the highest T_c—they discovered giant electron-phonon interactions. For this work, Cardona received the Excellence Award for Superconductivity at the 1992 World Congress on Superconductivity, which was held in Munich.

Cardona retired officially from the MPI in 1999, when he reached 65. However, he remained active in research there until the day he died. Among the projects he worked on after retirement, the one involving isotopically pure Si is worthy of special mention. Cardona's interest in the electronic band structure and vibronic properties of solids, and how these properties are tied to their optical properties, led him to be one of the early investigators in the field of host-isotopic effects.

For semiconductors and insulators, isotopes are expected to affect the phonon properties only. Cardona realized early on, however, that by studying isotopically pure samples one could isolate the effect of phonons, in turn, on the electronic properties of solids. For example, the influence of electron-phonon interactions on the band gap could be determined in this way. The study of isotopic effects in solids received a huge impetus from the end of the Cold War in 1991. Before that time, isotope effects had been studied typically in small-Z atoms such as H and O (for example, by replacing ^{16}O by ^{18}O in the HTS) because it was extremely difficult and expensive to obtain isotopically pure elements of higher Z. But an unusual opportunity occurred after the fall of the Berlin Wall in 1989. Strategic stockpiles of highly enriched and stable isotopes became commercially available from Russia for prices that made bulk crystal growth feasible.

Cardona was particularly fond and proud of his efforts to "beat…swords into ploughshares." He took advantage of Germany's location in Europe to host a number of former Soviet scientists at a time when many of them had suddenly been impacted by a loss of income and research resources.

Cardona was particularly fond and proud of his efforts to "beat…swords into ploughshares." He took advantage of Germany's location in Europe to host a number of former Soviet scientists at a time when many of them had suddenly been impacted by a loss of income and research resources. A number of the resulting investigations involved phonons in isotopically pure bulk-semiconductor crystals grown at the MPI. For example, for many years the phonon dispersion of Cd chalcogenides could not be measured by neutron scattering because natural CdSe contained too much ^{113}Cd, which has a large neutron-absorption cross section. Using isotopically pure Cd, Cardona's group measured the phonon dispersion curves of ^{114}CdS, $^{116}CdSe$, and $^{114}CdTe$ by neutron scattering for the first time. Another example was his use of isotopically pure samples to explain the anomalous Raman line shape of the transverse optical (TO) phonon in GaP.

With his collaborators, Cardona started a comprehensive study of the isotopic effects on the electronic properties of a wide variety of crystals. He started by collaborating with Eugene Haller at the University of California and the Lawrence Berkeley National Laboratory at Berkeley. Using all the stable isotopes of Ge obtained by Cardona from Russia, Haller grew extremely pure and isotopically enriched Ge crystals. Cardona and his team then determined precisely, from optical studies of these crystals, the contribution of electron-phonon interaction to the band gap (an effect known as renormalization) of Ge.

After 2000, Cardona's interest in host isotopic effects focused on Si, which is one of the most thoroughly studied and certainly the most economically important semiconductor. In his earlier studies, he had concentrated on the isotopic effects on the phonon spectrum and thermal conductivity of Si, which brought him into contact with Michael Thewalt of the Simon Fraser University in Burnaby, Canada. Their collaboration eventually turned to the studies of the optical properties of Si, and they became involved with the international Avogadro Project, whose goal was to redefine the kilogram based on precise measurements of the lattice constant and density of pure and isotopically enriched ^{28}Si. This project remains the source of the highest-quality bulk ^{28}Si single crystals even up to mid-2016, when this article was written.

In 2001, Cardona and Thewalt discovered that in the absence of disorder-induced broadening arising from isotopic defects, the line widths of a broad variety of optical transitions in ^{28}Si were far sharper than those observed in natural Si. As a result, they found that electronic transitions between the ground and excited states of donor and acceptor impurities in Si were not lifetime-broadened, as had previously been assumed. Without the inhomogeneous broadening due to isotopic defects, many hitherto-undetected effects became observable. For example, in the limit of the absolute temperature (T) approaching zero, they found that the energy of all direct inter-band electronic transitions in Si would vary as the *fourth power* of T.

Cardona and Thewalt showed that the derivation of this new result was quite similar to Debye's T^3 law for heat capacity of insulators at low temperature and hence should be applicable to all insulators. They also found that the hyperfine splitting due to the interaction of the donor electron spin with its nuclear spin could be resolved for the first time in the optical spectra of donor-bound excitonic transitions. The very old puzzle of the "intrinsic" splitting of the acceptor ground state in Si was finally explained by the isotopic inhomogeneity present in natural Si. The two scientists' remarkable results with ^{28}Si crystals have deepened our understanding not only of the basic physics of pure Si but also of the properties of common dopants in Si. Because donors and acceptors in Si play such an important role in the electronics industry, his body of work on this material is another example of Cardona's legacy both to semiconductor physics and electronics technology.

SELECTED BIBLIOGRAPHY

1960 With W. Paul and H. Brooks. Dielectric constant measurements in germanium and silicon as a function of temperature and pressure. In *Solid state physics in electronics and telecommunications,* Vol. 1. pp. 206. New York: Academic Press.

1961 Fundamental reflectivity spectrum of semiconductors with zincblende structure. *J. Appl. Phys.* 32:2151.

1962 With G. Harbeke. Excitons at the L-absorption edge in zincblende-type semiconductors. *Phys. Rev. Lett.* 8:90.

1963 Band parameters of semiconductors with zincblende, wurtzite, and germanium structure. *J. Phys. Chem. Solids* 24:1543.

1964 With B. Rosenblum. Evidence for normal regions at low temperature in the superconducting mixed states. *Phys. Rev. Lett.* 12:657.

With G. Fischer and B. Rosenblum. Microwave surface impedance of hard superconductors: In-Bi alloy. *Phys. Rev. Lett*. 12:101.

1965 With K. L. Shaklee and F. H. Pollak. Electroreflectance at a semiconductor-electrolyte interface. *Phys. Rev. Lett*. 15:883.

1966 With F. H. Pollak. Energy band structure of germanium and silicon: The k.p method. *Phys. Rev.* 142:530.

With F. H. Pollak and K. L. Shaklee. Piezo-electro reflectance in GaAs. *Phys. Rev. Lett.* 16:942.

1969 Modulation spectroscopy. In *Solid state physics.* Edited by F. Seitz, D. Turnbull, and H. Ehrenreich. New York: Academic Press.

1970 With W. Gudat, E. E. Koch, M. Skibowski, B. Sonntag, and P. Y. Yu. Core transitions and density of conduction states in the III-V semiconductors. *Phys. Rev. Lett.* 25:659.

With M. D. Maloney and F. de la Cruz. Anomalous behavior of Hc3/Hc2 near the Tc for Sn-In and In-Bi alloy systems. *Phys. Rev.* B 2:2512.

1971 With F. de la Cruz and M. D. Maloney. Superconductive supercooling and superheating of small cadmium spheres: Size effects. *Phys. Rev. B* 3:3802.

1990 With B. Friedl and C. Thomsen. Determination of the superconducting gap in RBa2Cu3O7-delta. *Phys. Rev. Lett.* 65:915.

1993 With P. Etchegoin, H. D. Fuchs, and P. Molinàs-Mata. Effects of isotopic disorder and mass on the electronic and vibronic properties of three-, two-, and one-dimensional solids. *J. Phys. Condens. Matter*. 5:A61.

Recent results in Raman spectroscopy of high Tc superconductors. *J. Phys. Chem. Solids* 54:1287.

1997 With R. Henn, T. Strach, and E Schönherr. Isotope effects in the optical phonons of YBa2Cu3O7: Eigenvector and infrared charge determination. *Phys. Rev. B* 55:3285.

1998 With C. Bernhard, R. Henn, A. Wittlin, M. Kläser, T. Wolf, G. Müller-Vogt, and C. T. Linn. Electronic c-axis response of Y1-xCaxBa2Cu3O7-delta crystals studied by far-infrared ellipsometry. *Phys. Rev. Lett.* 80:1762.

2002 With D. Karaiskaj, M. L. W. Thewalt, T. Ruf, and M. Konuma. Photoluminescence studies of isotopically enriched silicon: Isotopic effects on the indirect electronic band gap and phonon energies. *Solid State Commun.* 123:87.

2004 With T. A. Meyer and M. L. W. Thewalt. Temperature dependence of the energy gap of semiconductors in the low-temperature limit. *Phys. Rev. Lett*. 92:196403.

2005 With M. L. W. Thewalt. Isotope effects on the optical spectra of semiconductors. *Rev. Mod. Phys.* 77:1173.

2008 With A. H. Romero, R. K. Kremer, R. Lauck, G. Siegle, J. Serrano, and X. C. Gonze. Lattice properties of PbX (X=S, Se, Te): Experimental studies and ab initio calculations including spin-orbit effects. *Phys. Rev. B* 78:224302.
