Quasicrystal Discovery—From NBS/NIST to Stockholm[a]

Balazs Hargittai[b] and István Hargittai[c]

Abstract

There were ideal conditions in 1982 at the NBS/NIST for the kind of exploratory research that led Dan Shechtman to the quasicrystal discovery. Almost 30 years later, in 2011, Shechtman received the Nobel Prize for this achievement. What happened in between these two dates has been covered quite extensively elsewhere. But it is intriguing to learn more about the very beginning. Then, the festivities in Stockholm added to our seeing the story in a fuller perspective.

Keywords

Quasicrystals • Dan Shechtman • Quasiperiodicity • NIST • Nobel prize

Many aspects of the quasicrystal story have been covered (see, e.g., [1–4]), but very little has been described of the circumstances of the original discovery, which happened at the (then) National Bureau of Standards, NBS—today's National Institute of Standards and Technology, NIST—in Gaithersburg, Maryland.

In 1981, Dan Shechtman of the Technion—The Israel Institute of Technology—went for his first sabbatical at NBS. His stay at NBS had been initiated by a senior scientist there, John Cahn, because of his interest in a technique Shechtman had developed for studying metallic powders by transmission electron microscopy. Shechtman's work at NBS was sponsored by the then U.S. Defense Advanced Research Project Agency (DARPA). Shechtman remembered that Jake Jacobson of DARPA told him specifically not to limit his studies to his originally proposed plan but rather to expand in any direction he felt was interesting. Shechtman further remembered in a conversation in 1995 during an international school on quasicrystals: "I started by studying rapidly solidified aluminum-iron alloys. I analyzed the phases present and the solidification patterns. I collaborated mainly with members of the metallurgy group, Bill Boettinger, Bob Schaefer and Frank Biancaniello. We wrote a series of papers together and understood rapid solidification better. It was in April 1982, half a year after I had arrived, that I discovered the icosahedral phase" [5].

This conversation was part of an extensive project, which included interviews of some other scientists who figured in the quasicrystal story (Fig. 1).

Frank Biancaniello's role was especially important in Shechtman's studies. Biancaniello was not yet a full-fledged researcher at the time (as he has become soon afterwards); he was, rather, a technician whose task included the preparation of the alloy samples of various compositions for the electron microscope–electron diffraction experiments. Biancaniello was—according to the testimony of the other members of the group—most enthusiastic about this investigation. He was happy to work many extra hours, including nights and weekends, and he was as skilled as he was devoted to this project. This is how the tests continued outside the range of reasonable compositions—reasonable, that is, for expected practical

[a] *Structural Chemistry* 2012, 23(2):301–306.

[b] Department of Chemistry, Saint Francis University, P.O. Box 600, Loretto, PA, USA
e-mail: bhargittai@francis.edu

[c] Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, P.O. Box 91, Budapest 1521, Hungary
e-mail: istvan.hargittai@gmail.com

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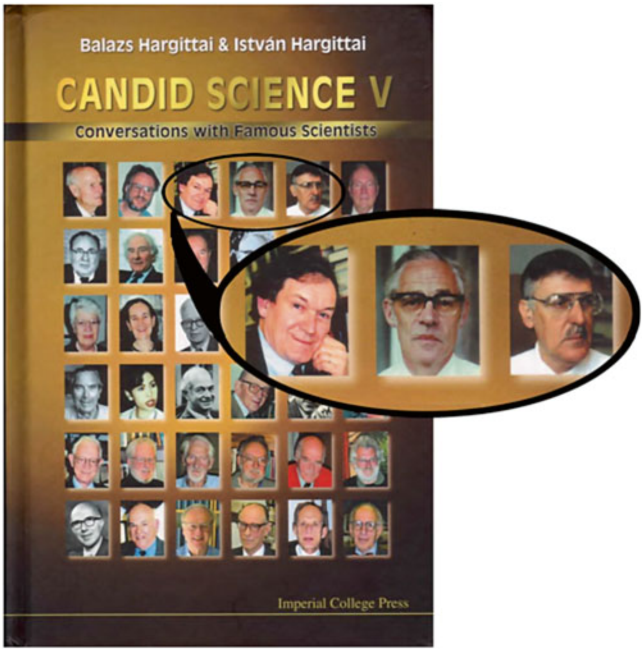

Fig. 1 A collection of interviews containing conversations with a few of the principal players of the quasicrystal story. Portraits of Roger Penrose, Alan Mackay, and Dan Shechtman are highlighted.

applications. Biancaniello remembers, "Obviously, the quasicrystal discovery was the most important one culminating in Danny's Nobel. But there were many other exciting projects we worked on that came to fruition over the years. I'm sure you have heard of some of the bulk metallic glass research being carried out over the years, with yield strengths on the order of 1 to 2 gigapascals with no ductility. Steve Ridder and I developed a High Nitrogen Stainless Steel with a yield strength of 1.1 gigapascals with an elongation of 60% using so-called rapid solidification technology. I only mention this in an attempt to demonstrate how intellectually stimulating these thirty years were starting with working with Danny Shechtman and continuing on to recent times. As Bill Boettinger mentioned, we worked on many projects with Danny. Steve Ridder and I did more recent research with Danny using a quasicrystal for a wear-resistant coating while doing thermal spray studies" [6].

Shechtman narrated in the 1995 conversation about some of the details of the seminal experiment [7]:

> At first, I was studying rapidly solidified aluminum-iron alloy, which we thought had some commercial future. Eventually, it turned out that although rapid solidification research resulted in several useful products, it did not develop into a widespread technology. This, however, is not important for our story. In the aluminum-iron binary system there was one metastable phase Al_6Fe, which I studied. The equivalent Al_6Mn in the aluminum-manganese system is a stable phase, and I wanted to compare some crystallographic features of the two. We started therefore to produce a series of aluminum-manganese alloys with increasing amounts of Mn in them. Eventually I ran wild, from a practical point of view, since beyond several percents of manganese the rapidly solidified alloy becomes brittle and therefore useless. Among the alloy ribbons which I have prepared with Frank Biancaniello by melt spinning, there were alloys which contained over 25 weight percent manganese. On April 8, 1982, as I was studying by electron microscopy rapidly solidified aluminum alloy which contained 25% manganese, something very strange and unexpected happened. It is worthwhile to look at my TEM [transmission electron microscope] logbook records of that day. For plate number 1725 (Al-25% Mn) I wrote: "10 Fold ???"
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> There were ten bright spots in the selected area diffraction pattern, equally spaced from the center and from one another. I counted them and repeated the count in the other direction and said to my self: "There is no such animal". In Hebrew: "Ein Chaya Kazo". I then walked out to the corridor to share it with somebody, but there was nobody there, so I returned to the microscope and in the next couple of hours performed a series of experiments. Most of the needed experiments were performed at that time. A few days later all my work was complete, and everything was ready for the announcement. Then it took two years to publish it.

The diffraction pattern with bright spots indicating tenfold symmetry in the solid structure is reproduced in Fig. 2 and the logbook page where the observation of the conspicuously unexpected pattern is recorded is reproduced in Fig. 3.

Shechtman almost immediately excluded the possibility that the pattern originated from crystal twin formation—something that many crystallographers first suspected upon becoming acquainted with Shechtman's observations. Of course, Shechtman could not dismiss such a supposition off hand. Rather, he had prepared himself for such a question, the more so, because this possibility had also occurred to himself. In his words, [referring to the fact that the sequence of distances of the bright spots from the central spot was not periodic in his observation] "When an electron microscopist sees such a sequence the first thought is that these must be

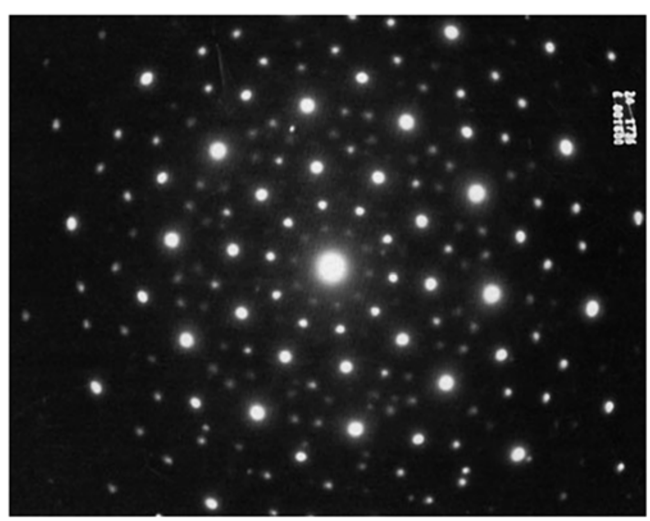

Fig. 2 Shechtman's historic electron diffraction image of the aluminium/25%-manganese alloy (Courtesy of Dan Shechtman).

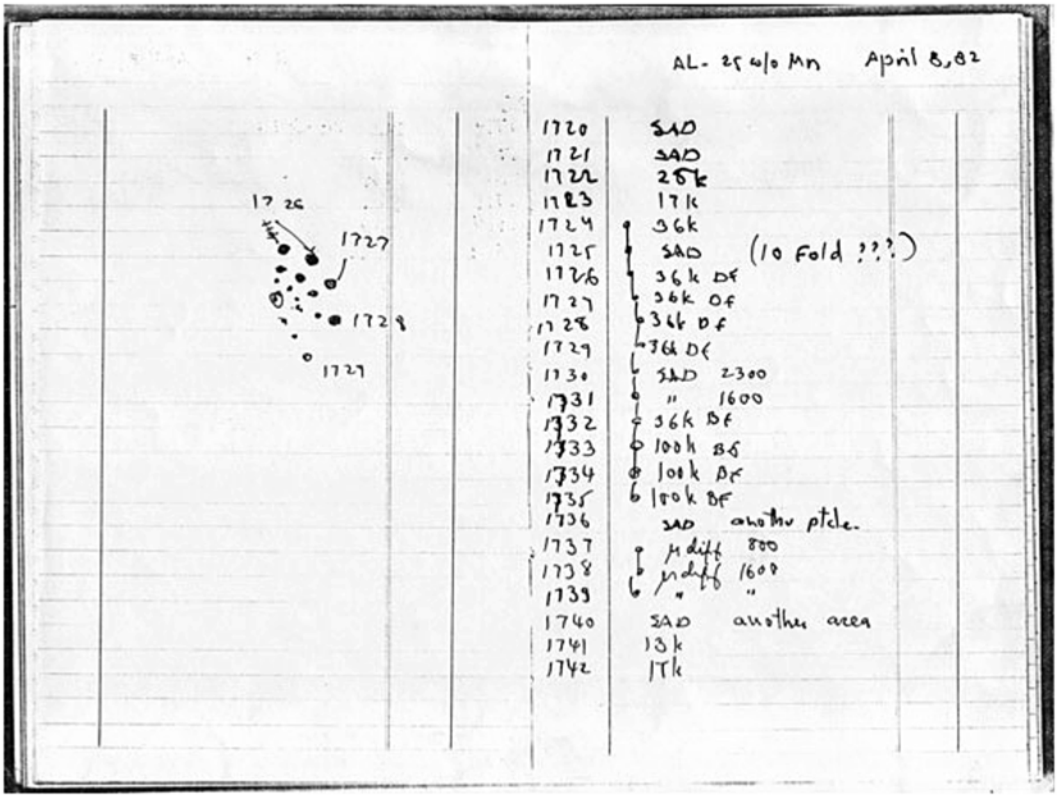

Fig. 3 Page in Shechtman's logbook where he recorded his observation of tenfold symmetry of plate 1725 on April 8, 1982, with highlighted information (Courtesy of Dan Shechtman).

twins. The alternative explanation is single crystal icosahedral symmetry, which was assumed to be forbidden symmetry for crystals although for molecules this symmetry has been known to exist. In order to prove that my diffraction patterns did not originate from twins, I generated a series of dark field images. In these experiments you take an image from a diffracted point such that all the information that passes to the plate is contained in the beam only. Examining the information I have found that the dark field images were almost identical which means that the same part of the crystal produced all the diffracted beams. It was clear to me that the crystal, the origin of diffraction was not twinned" [8].

When Shechtman mentioned that "it took two years to publish" his observation, this was an understatement, because it took more than two and a half years. But the delay was not only due to the disbelief of the scientific community that the dogma about the impossibility of fivefold symmetry (and other "forbidden" symmetries) should fall. It was also a delay of Shechtman's own making. Of course, the resistance of the scientific community bothered him and he would have liked to come out with a suitable model along with the publication of his observation. By mid-1984, however, he realized that he should have his observation printed in the scientific literature and produced a manuscript in co-authorship with Ilan Blech. They submitted their manuscript to the Journal of Applied Physics in the summer of 1984. The manuscript was more of the nature of a report in metallurgy than in physics and this may be judged as being so because eventually about the same manuscript appeared in a metallurgy journal [9]. The manuscript to Journal of Applied Physics was submitted in the summer of 1984 and the editorial decision came back soon. According to the letter two items were enclosed with it, the original manuscript (Ms. #R-6168) and a Reviewer's report. The Reviewer's report could not be found and Shechtman does not remember having seen such a report [10]. The Editor of Journal of Applied Physics, Lester Guttman said, "Our reviewer and we both believe that your paper will not reach the most appropriate audience through this journal, and we are therefore returning your manuscript. We wish to make it clear that this is not a comment on the technical quality of your work; rather it is an attempt on our part to try to place papers where they will be of the greatest use to the greatest number of people."

Even before Shechtman received the letter of rejection, he showed the manuscript to John Cahn who described his reaction to one of us, in a conversation in 1995 in Gaithersburg [11]:

> I read this paper immediately, and got very excited, because I saw the data for the first time. I wasn't convinced by the Blech model, but I was very much convinced by the experiments. It was obvious that it was not twinning, that it was something outside of what was known. I'm sure that had I seen the data in '82 the same day when they were taken, we wouldn't have wasted

> 2 years. On Friday I met with Danny and said, this is a poorly written paper, you're hiding this new phase. The entire paper was about experiments on aluminum–manganese. It started out by saying that we did this, we found this, and gave a list of the known periodic phases for each composition range, and buried, in half a paragraph, was a new phase, in the middle of an otherwise very conventional paper. My impression was that it was written that way to sneak it pass the referee, because everybody, except Blech, had told him that he had nothing.
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> I remember that Friday going to the bosses and telling them that this is really something and it's going to be big. I more or less said that we should mount a major effort; lots of people should shift because this has got to be investigated. At this stage I was not a co-author and I did not expect to be a co-author. I told Danny that this is the wrong paper but Danny told me that the paper had been submitted.

By the time Shechtman and Cahn talked again, the manuscript had been rejected by the Journal of Applied Physics and submitted to Metallurgical Transactions. Cahn still thought that this was the wrong manuscript and said so to Shechtman. At this point, Shechtman told Cahn if he thought so strongly about it he should write the right manuscript. This is how the paper that finally made the breakthrough was initiated [12]. When the manuscript was ready there was still another hurdle to overcome before it could be submitted for publication. This is how Cahn remembered [13]:

> At NIST we have an Editorial Review Board. Every paper from the Institute has to be reviewed internally before it can be sent out. This Review Board was afraid of another polywater. The Bureau of Standards had been burned by polywater publications. The Board wanted to be on the right side this time and had asked local crystallographers to give them lectures about fivefold symmetry, why it can't be. They were spending a great deal of time. The Board was split. My Division Chief of Metallurgy, also an old friend, said to me, "John, you have a wonderful reputation. Why ruin it by putting your name on something like such a paper." I said, "please, read this paper, it is very important and very exciting, and it's not a time to be conservative." The Board took a very long time, they had lots of meetings, sometimes they came to me for advice but I was never present at these meetings. They carried an inquiry very carefully, and eventually they approved the paper. Finally, in mid-October [1984], we could send off the manuscript. It came out 3 weeks after it was submitted.

NIST followed up Cahn's recommendation in forming a quasicrystal group to conduct experimental as well as theoretical work. For a while, the outside world considered NIST to be in the focal point of this new field and researchers kept sending the NIST group their manuscripts, about 300 preprints already in the first year (Fig. 4).

On November 3, 2011, the authors of this Editorial visited the Metallurgy Division at NIST and at their request met with the associates of NIST who had been Shechtman's colleagues at the time of the quasicrystal discovery. At this informal meeting, present was the current Chief of the Metallurgy Division, Frank Gayle. The very friendly

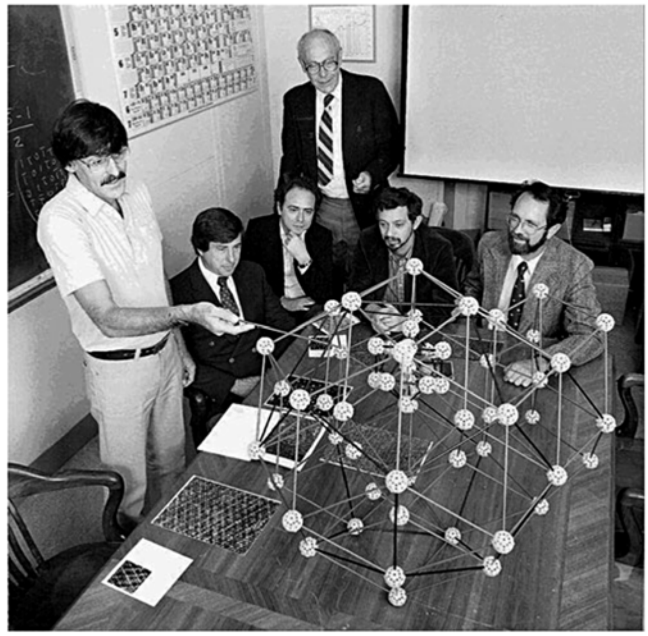

Fig. 4 In 1984, at NBS, Dan Shechtman, Frank Biancaniello, Denis Gratias, John Cahn, Leonid Bendersky, and Robert Schaefer (Photograph: H. Mark Helfer/NIST; Courtesy of NIST).

sentiments toward Dan Shechtman shone through this gathering; the reminiscences made it obvious that the helpful and creative atmosphere in the group must have greatly facilitated the birth of new experiments and new ideas. One of us has written about the loneliness of the scientific discoverer, which their supportive collective spirit which must have at least eased Shechtman's scientific loneliness (Fig. 5). stems from the fact that the discoverer knows something—for a while anyway—that nobody else does and sometimes has to go against the mainstream of science; this was the case of the quasicrystal discovery. However, in a human sense, socially, Dan Shechtman was never alone in this community and his former colleagues take pride in the strength of their supportive collective spirit which must have at least eased Shechtman's scientific loneliness (Fig. 5).

Eventually, Dan Shechtman being primarily at the Technion, his principal research activities moved there. He did not immediately focus his further studies on quasicrystals, but he never abandoned the area entirely. In the press conference during the Nobel festivities in December 2011 he was relaxed about the period of frustration when he had been waging an uphill battle in the scientific community for the recognition of his discovery. Incidentally, among the many awards he received for his achievement, the Georgi Aminoff Prize in 2000 was very special, because it is given by the same institution as the chemistry Nobel Prize, the Royal Swedish Academy of Sciences. The motivation was "for your discovery of quasicrystals." Those of us who were present at his Aminoff lecture in 2000 and at his Nobel lecture on

Fig. 5 From left to right, Istvan Hargittai, William Boettinger, Frank Gayle, Francis Biancaniello, Stephen Ridder, Leonid Bendersky, Robert Schaefer, and Balazs Hargittai at NIST on November 3, 2011.

December 8, 2011, could notice the similarities between the two presentations. This was no accident; the motivation of his Nobel Prize was the same by the same institution, "for the discovery of quasicrystals." In his Nobel lecture, Shechtman made an effort to avoid using the name "quasicrystal" and preferred "quasiperiodic crystal" instead, though the term "quasicrystal" slipped through several times (Figs. 6 and 7). In 1995, he explained the difference: "At least some of the materials we call quasiperiodic crystals can be explained by quasiperiodic tiling of space. Others can be explained by the icosahedral glass model. The general term quasicrystal, coined by Dov Levine and Paul Steinhardt, is a nice popular term but it does not say scientifically what it is. In addition, the term quasicrystallographer, for example, is not acceptable; quasiperiodic crystallographer may sound better" [14].

At the award ceremony, Sven Lidin, Member of the Royal Swedish Academy of Sciences and Member of the Nobel Committee for Chemistry in his presentation speech pointed out the importance of observations in making and breaking theories. The discovery of quasicrystals did away with the dogma that periodicity was a prerequisite for crystallinity. Much of his presentation speech was about a metaphor of the dwarf and the giant that has been known from antiquity but made most famous by Isaac Newton, according to which if the dwarfs sees farther it is because he stands on the shoulder of giants. The giant is the accumulated knowledge and the dwarf is the discoverer. As Lidin put it, "The giant provides established truths. The dwarf strives for new insight." The connection to the 2011 Nobel Prize was obvious in that Shechtman was the discoverer and he was standing on the foundation of accumulated knowledge, but saw farther (Figs. 8 and 9). Lidin stressed that the metaphor also hinted at the dangers of this arrangement [15]:

> The relation between the dwarf and the giant is fundamentally asymmetric. The dwarf can see, but the giant decides on which road the two shall take. The dilemma of the giant is that he is at the mercy of the dwarf, but he cannot trust him blindly. The paradigms of science are challenged daily on more or less solid grounds and the difficulty is to know when to take these challenges seriously. The dwarf faces the reverse problem. He depends on the giant, and without him he gets nowhere despite the clarity of his vision. In order to make his own choices he is forced down on the ground, to walk alone without the support he enjoyed on the shoulders of the giant. … The dwarf doesn't serve the giant by subservience but through independence.

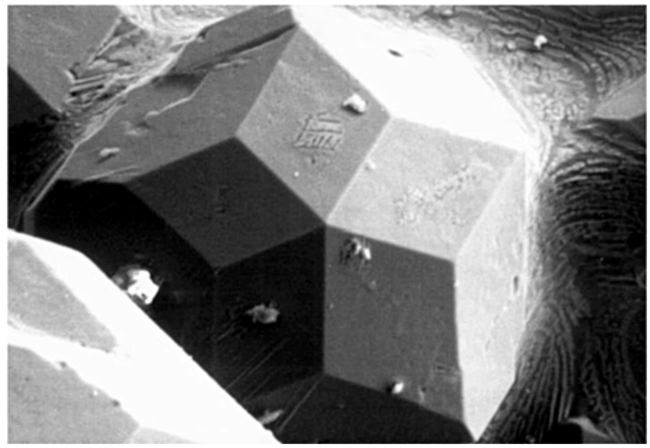

Fig. 6 From among the quasicrystal images produced at NIST: triacontahedral Al-Cu-Li quasicrystal (facet edges about 100 μm long) by Frank Gayle.

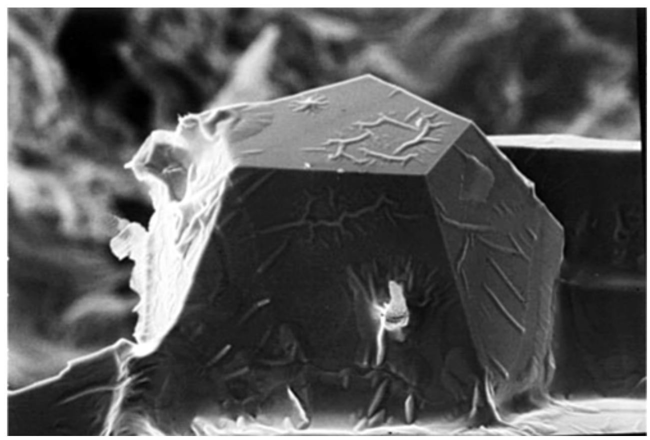

Fig. 7 From among the quasicrystal images produced at NIST: dodecahedral Al-Cu-Fe quasicrystal (facet edges about 100 μm long) by Frank Gayle.

Lidin called the disbelief with which the scientific community initially met the scientific discovery healthy, but the ridicule to which Shechtman was subjected, deeply unfair. In addition to having created a new branch of science, Lidin found great achievement in that the quasicrystal discovery "has given us a reminder off how little we really know and perhaps even taught us some humility."

Fig. 8 Dan Shechtman at the press conference on December 7, 2011, Royal Swedish Academy of Sciences (Photograph by Istvan Hargittai).

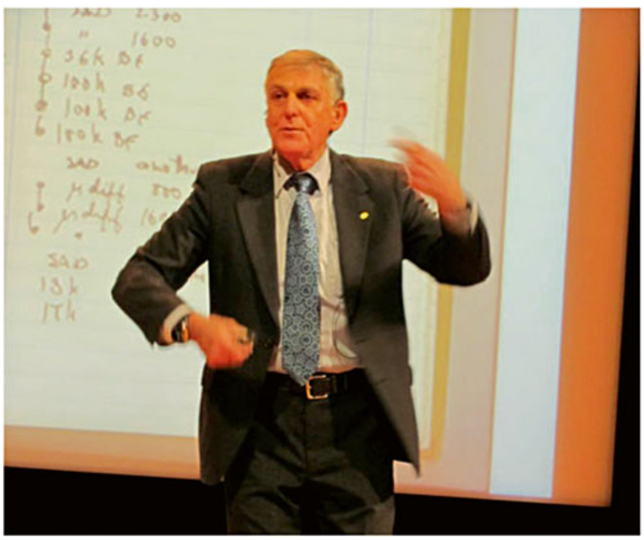

Fig. 9 Dan Shechtman during his Nobel lecture on December 8, 2011, in Stockholm (Photograph by Istvan Hargittai).

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