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EDITORIAL

Forty years of quasicrystals: a bumpy road to triumph

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Abstract

On April 8, 1982, Dan Shechtman conducted an electron diffraction experiment on an aluminum/manganese alloy. The diffraction pattern showed tenfold symmetry although the rules of crystallography excluded such symmetry in extended structures. Alan L. Mackay had anticipated such structures, which fit his view of generalized crystallography. Shechtman persisted in claiming to have observed quasiperiodic structures despite denial of such structures even by Linus Pauling, the greatest authority in chemistry. When Shechtman's claim was finally accepted, he was amply awarded for his contribution, including his Nobel Prize in 2011. The theoretical physicists Paul J. Steinhardt and Dove Levine coined the name quasicrystals, and advanced the field greatly by their models, but appeared to downplay somewhat the significance of prior predictions and of the experimental discovery.

Keywords Dan Shechtman · Alan L. Mackay · Linus Pauling · Paul J. Steinhardt · Dov Levine · Quasiperiodic structures · Quasicrystals · Rules of crystallography

Forty years ago, on April 8, 1982, Dan Shechtman of the TECHNION, at that time a visiting scientist at the National Institute of Science and Technology (formerly, the National Bureau of Standards in Washington, D.C.), made a startling observation (Fig. 1): when he shone an electron beam onto a sample of an aluminum/manganese alloy of 25% manganese content, the electron diffraction pattern showed tenfold symmetry.

Shechtman's observation contradicted a long-accepted dogma of classical crystallography that fivefold—and its multiplies—symmetry could not exist in extended structures. Yet, Shechtman did not dismiss this observation as impossible. First, he thought that the diffraction pattern was an evidence of a twinned crystalline structure and spent the rest of that afternoon trying to find the twins by a series of dark field experiments ("DF," Fig. 1) and micro-diffractions ("μdiff," Fig. 1). The twins were not there. He concluded that the symmetry of the diffraction pattern was coming from the atomic order of the crystal itself.

Shechtman proved on the day of the discovery that the diffraction pattern did not result from a twinned crystal. He completed all the experimental work in a few hours' time, which would overthrow a heretofore inviolable dogma of crystallography, though by far not instantly [1]. To the actual acceptance of the discovery, there was a long road, and even longer for its rewards. The difficulties in accepting Shechtman's discovery is even more puzzling if considering that, although unbeknownst to Shechtman, Alan L. Mackay of Birkbeck College, London University, had anticipated the existence of fivefold symmetry in extended structures. Mackay argued that there should be rules for generating such structures, and they should not necessarily be periodic. He began publishing his teachings under the title "generalized crystallography" as early as 1975 and continued over the next decades [2–9]. Mackay even arranged for generating a diffraction experiment on a Penrose pattern—a two-dimensional extended structure of fivefold symmetry [5]. By the way, both Roger Penrose [10] and Mackay combined playing—doodling, for example—and hard science. The following episode illustrates Mackay's playfulness. The Soviet crystallography periodical *Kristallografiya* invited him to contribute to the celebration of the crystallographer Boris K. Vainshtein's anniversary. Mackay created a graphical representation of a snowflake of fivefold symmetry [4]. There was a postal strike in Britain at the time and his manuscript might have not made it in time for the celebratory issue. Ever unconventional, Mackay threw his manuscript over the gate of the Soviet Trade Mission in Highgate, London, and his paper got there in time.

I was familiar with Mackay's teachings, first from his papers, and in 1982 we invited him for a visit to Budapest.

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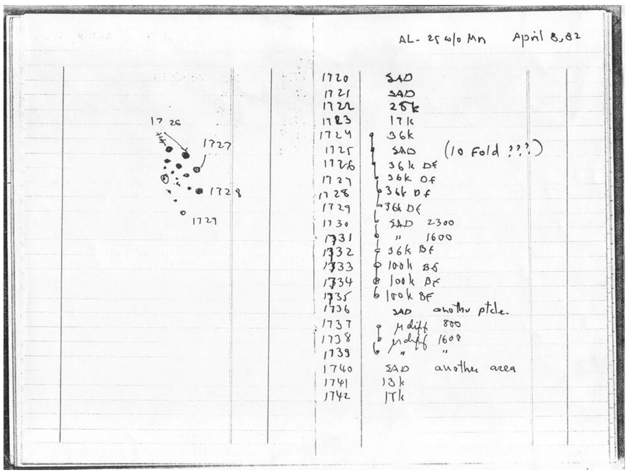

Fig. 1 The page in Dan Shechtman's lab diary—his transmission electron microscopy (TEM) notebook—referring to the date, April 8, 1982, and to the composition of the aluminum/manganese alloy, he was examining on that day, of 25% manganese content. Pattern 1725 is distinguished by "10 Fold ???". Reproduced by courtesy of and with permission from Dan Shechtman

He gave three lectures, two of which were titled and focused on fivefold symmetry. In September 1982, he told us that we should be aware of the possibility of fivefold symmetry in extended structures. If we thought them impossible, they might go by us unnoticed and unrecognized. As Mackay talked to us about this, Shechtman had already observed such structures. Incidentally, Mackay's simulated diffraction pattern turned out to be fully consistent with Shechtman's actual diffraction pattern [11]. Although Shechtman was not familiar with Mackay's warning, he did recognize his diffraction pattern for what it was, and when others dismissed it, he stuck to his initial interpretation of his observation. On his part, his perseverance turned out to be as important as making the observation in the first place [12].

In Linus Pauling (1901−1994), Shechtman had a formidable opponent on the road to having his discovery recognized. In his prime, Pauling himself was not only a discoverer but also a brave innovator. Suffice it to remember his successful quest leading to the discovery of the alpha-helix structure of proteins [13]. Pauling's words carried weight not only for his leading position in chemistry in general, but also due to his prior successes in the understanding of icosahedral structures. He maintained to the end that what had been described as quasicrystals in the literature were twin formations of large crystals. Pauling published one of his examples in 1989 in one of my edited symmetry volumes [14]. A few years later, in Fall 1993—as it turned out, it was shortly before his passing—I asked him about quasicrystals. His answer showed that he had not changed his mind: "You know that I contend that icosahedral quasicrystals are icosahedral twins of cubic crystals containing very large icosahedral complexes of atoms. It is not surprising that these crystals exist. The first one to be discovered was the MgZnAl compound reported by my associates and me in 1952. We did not observe quasicrystals of this compound, but they have been observed since then." [15] Here, Pauling's use of the name "quasicrystals" meant the icosahedral twins of cubic crystals. For the chemistry community, including the crystallographers, it was easier to recognize Shechtman's discovery after Pauling was no longer around.

Shortly after Shechtman and his colleagues communicated the experimental discovery referred to above [1], Dov Levine and Paul J. Steinhardt (then at the University of Pennsylvania; now, at Princeton) suggested a theoretical model interpretation of Shechtman's discovery [16]. This was an important step ahead in understanding these heretofore unknown or, rather, unrecognized, structures, the more so as Shechtman's first attempts to understand them were not very successful [17]. I found the Levine-Steinhardt paper very interesting, not the least, because they coined the name: quasicrystals. An intriguing feature of this paper was the order of references, meaning the order in which previous works were considered in their narrative.

There could be little doubt that the publication of the paper on modelling was inspired by Shechtman et al.'s recent report [1], yet it was referred to quite late in the paper. Mackay's prior work was also mentioned, but only in passing and at the very end. This looked strange and, many years later, I asked Levine about it. At the time of the quasicrystal discovery, Levine was Steinhardt's doctoral student. When I recorded my conversation with Levine in Spring 1996, he was a Senior Lecturer at the Department of Physics of the TECHNION. The entrance lobby of this department has a Penrose pattern-like floor decoration (Fig. 2). The conversation was part of a large piece in which I communicated my interviews with some of

Fig. 2 Penrose-pattern-like floor decoration in the lobby of the Department of Physics at the TECHNION (photograph by I. Hargittai)

the principal players of the quasicrystal saga: Alan L. Mackay, Dan Shechtman, John W. Cahn, Dov Levine, Paul J. Steinhardt (this was by correspondence), and Marjorie Senechal. I am quoting here verbatim, both my question to Levine about the order of references in the Levine and Steinhardt paper [16] and his response [18]. The magazine, *The Chemical Intelligencer*, in which this set of conversations appeared, stopped publication at the end of 2000.

> Question (IH): "Scrutinizing your paper (here, [15]), my impression is that it seems as if you were a little bit downplaying the importance of Shechtman et al.'s paper (here, [1]). Obviously your paper was written in the wake of Shechtman's discovery, yet one has to read quite a bit into your paper before this work is mentioned. It is the number 10 reference out of a total of 13. Mackay's prediction, being referred to almost indirectly, comes in as the last reference."
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> Dov Levine's response: "Of course, I don't remember all the details. As for Alan Mackay's contribution, we didn't find it conclusive and we didn't quite figure out how to deal with it. He did have a diffraction picture and we mention it. What he said in essence was that it would be great if it were true, if this happened. But this is not a prediction. He had a wonderful imagination, and he deserves a lot of credit for it.
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> My recollection is the following. Paul [Steinhardt] was concerned that we were going to get the label of a couple of smart guys who saw the experiment and jumped in. We wanted to stress that this was not the case. I suspect that that was the idea of not starting with the remarkable experiment by Shechtman et al. because that would have led to that (wrong) impression. I think that's the reason that Danny is number 10. We weren't trying to downplay it. Our general approach was, and it was a long time ago, to try to give the correct impression that we had been working in the field for two years and we weren't just a couple of guys who saw the experiment and quickly put two and two together. The paper was written largely with that in mind. I think that any errors in *politesse* (manners) in attribution came out of that desire. There was certainly no desire to downplay the Shechtman paper. Certainly, in talks we gave we always made this very clear."

Alas, this was not the only time one could form the impression that Shechtman's and Mackay's contributions were downplayed. My other example goes back to January 1985, that is, only a few weeks after the appearance of Shechtman et al.'s paper [1] and the Levine and Steinhardt's paper [16]. The Science Section of the January 8, 1985, issue of *The New York Times* carried an article (p C2), titled "Theory of New Matter proposed." The account detailed the pioneering theoretical work at the University of Pennsylvania, but failed to mention Mackay's contribution. This prompted me (at the time I was a Visiting Professor at the University of Connecticut, Storrs) to send a "Letter to the Editor," on January 22, setting the record straight, concerning Mackay's contribution. As far as I know, the newspaper did not use the letter, but we reproduced it in full in our book, *In Our Own Image: personal symmetry in discovery* [19]. Soon after I sent the letter though, Mackay received a letter of January 28, 1985, from the Science Editor of *The New York Times*, stating that "The University of Pennsylvania press office should have made mention of your earlier contribution." [20]

The previous two examples go back to 1984−1985. In the meantime, Dan Shechtman has been recognized for his discovery with the Aminoff Prize in 2000 and the Nobel Prize in 2011. Also, Alan Mackay shared the Oliver E. Buckley Condensed Matter Physics Prize with Dov Levine and Paul J. Steinhardt in 2010. The motivation for the distinction read: "*For pioneering contributions to the theory of quasicrystals, including the prediction of their diffraction pattern.*" A recent example of downplaying Shechtman's and especially Mackay's contributions was exposed in Marjorie Senechal's eloquent essay [21] apropos of Paul Steinhardt's book, *The Second Kind of Impossible: the extraordinary quest for a new form of matter* [22].

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