

On the Density of Racemic and Homochiral Crystals: Wallach, Liebig and Sommerfeld in Göttingen

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Dedicated to Prof. Jack Dunitz on the occasion of his 95th birthday. In memoriam of Howard Flack

Abstract: The first comparison of heterochiral crystals with their homochiral counterparts was given by Otto Wallach in an account on carvone bromide crystals in 1895 in *Liebigs Annalen der Chemie*. Although the well-known mineralogist Theodor Liebig, professor in Göttingen from 1887 to 1908, performed the analyses and wrote the last four pages of that *Annalen* paper, his colleague from chemistry, Wallach served as sole author. We discuss whether Wallach or Liebig had the idea of a comparative study of crystal densities of racemates and their homochiral analogues and who of the two should be credited.

Keywords: Arnold Sommerfeld · Chiral crystallization · History of science · Otto Wallach · Theodor Liebig



Born in Northeim near Göttingen in Lower Saxony, Germany, **Karl-Heinz Ernst** was originally trained as Chemical Technical Assistant (CTA). He studied Chemical Engineering and Chemistry at the TFH Berlin and the Freie Universität Berlin, respectively. His PhD studies were conducted at the Berlin Electron Storage Ring for Synchrotron Radiation (BESSY I) and the Freie Universität Berlin. After a postdoctoral research stay at the University of Washington in Seattle he joined Empa,

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1. Introduction

In 1895 Otto Wallach published as sole author a paper entitled ‘*Zur Kenntnis der Terpene und der ätherischen Oele; No. 34: Ueber gebromte Derivate der Carvonreihe*’,^[1] in *Justus Liebigs Annalen der Chemie* 286, pp. 119–143.^[2] One important result of the paper is the evaluation of the density of racemate crystals with respect to their homochiral counterparts. For eight of the nine tested samples, higher densities (up to 4%) were reported for the racemate crystals. The empirical finding, namely, that racemic crystals tend to have a higher density than their homochiral analogues, was coined later ‘Wallach’s rule’,^[3] an expression which has subsequently often been used in the literature.^[4–8] As published previously in

an essay about this small episode of the history of science,^[9] it was Wallach’s colleague Theodor Liebig, professor of mineralogy in Göttingen, who performed and reported on the density of crystals of chiral compounds in the Wallach-authored *Annalen* paper. In the same paper, which even contains measurements performed by Arnold Sommerfeld, both Wallach and Liebig claimed to be the father of the idea of such comparative studies. Although it was common at that time not to have students and assistants listed as coauthors, it is quite interesting to speculate why Wallach did not include his colleague as a coauthor.

2. Otto Wallach (1847–1931)

Otto Wallach was born (27.3.1847) in Königsberg, East Prussia, and grew up in Potsdam near Berlin (Fig. 1). Due to health problems, he had a bad start in school,^[10] but became a good student later. His friend Georg Borsche introduced him to chemistry and Wallach followed him in 1867 to Göttingen to study chemistry under Friedrich Wöhler. He spent one semester inbetween in Berlin with August Wilhelm von Hofmann (1818–1892), who had just come from London as Eilhard Mitscherlich’s (1794–1863) successor. Wallach completed his PhD after only five semesters! In his doctorate work (‘Über von Toluol abgeleitete neue isomere Verbindungen’) under the direction of Hans Hübner, he isolated an unknown

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isomer of bromotoluene by crystallization. Although a true finding, it was disputed by Wöhler's assistant Fittig, who offered his head if Wallach were right. (“*Der Wallach will ein neues Bromtoluol gefunden haben! Ich lege meinen Kopf auf diesen Tisch und Sie können ihn abhauen, wenn das richtig ist.*”^[11] “*Wallach claims discovery of a new bromotoluene! I will lay down my head onto this table and you may decollate it, if this is correct.*”).

Wallach was happy to leave Göttingen in 1869, “*with the quiet and genuine desire: never to be seen there again.*”^[11] As Fig. 1 shows, it turned out differently. Wallach became assistant of Hermann Wichelhaus in Berlin and worked with August Kekulé in Bonn. After voluntary service in the German-French war, he went to Agfa in Berlin, but returned to Bonn again to work with Kekulé and achieved his Habilitation. As professor for pharmacy in Bonn, Wallach began his seminal terpene work. Wallach described later as cause for his interest in ethereal oils, flasks on a cupboard in Kekulé's private laboratory containing such substances, but being untouched for fifteen years. Wallach's request to perform research on their content were granted by Kekulé with ironical laughter: “*Yes, if you can make anything out of them!*”^[12]

In the 1880s research on terpenes had been lacking a systematic approach. Wallach: “*...if one casts a glance over the old literature of the terpenes, it does not appear a particularly enticing subject for investigation. There were isolated observations in almost incomprehensible abundance.*”^[13] Or in the words of Leopold Ružička (1887–1976, Chemistry Nobel laureate 1939): “*...Wallach had plunged into work in a neglected garden so over-run with weeds that the useful plants could not thrive. Any good gardeners had already attempted to improve its condition, but each had soon damaged his hands and the weeds had begun to flourish again with renewed vigor. [...] After about the beginning of 1890, the garden was well weeded and it soon enticed other gardeners to investigate the conditions of life and the properties of the plants, and to determine their species.*”^[12]

Wallach reported in 1888 that dipentene is nothing but the racemic mixture of limonene enantiomers,^[14] and managed to isolate (–)-limonene from spruce needle oil. As already had been applied in his doctoral work, Wallach brominated the compounds and achieved thus products that could be readily crystallized. As with Liebig later in Göttingen, he involved a mineralogist (Carl Adolf Ferdinand Hintze, 1851–1916) in his analyses. When Victor Meyer went to Heidelberg in 1889 to replace Bunsen, Wallach succeeded him and went back to Göttingen, where he continued his work

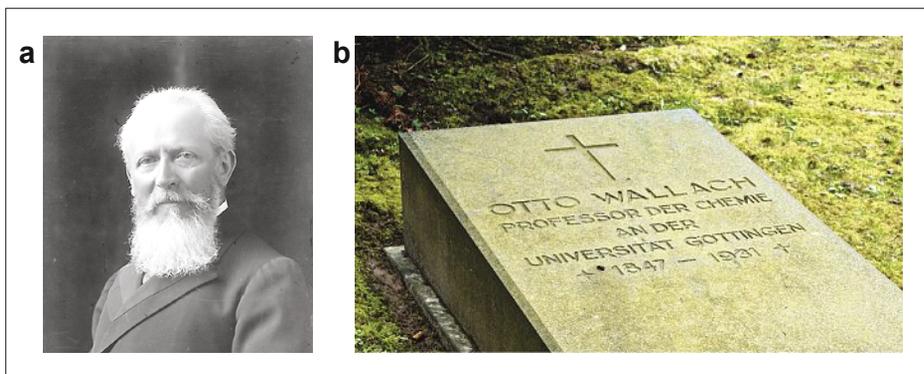


Fig. 1. a) Otto Wallach, Nobel Laureate in Chemistry 1910. b) Wallach is buried at the Stadtfriedhof in Göttingen among seven other Nobel laureates and many famous scientists and mathematicians.

on terpenes until his retirement in 1915. Wallach was very active even after his retirement and remained a bachelor his entire life. He was appointed already in 1885 fellow of the *Deutsche Akademie der Naturforscher Leopoldina*, which awarded him – long before Emil Fischer – with its prestigious Cothenius Medal. As fellow of the Prussian Academy of Sciences, Wallach became decorated with more medals by Prussia. His colleagues in England elected him as Honorary Fellow of the Chemical Society and awarded him the Honorary Doctor of the University of Manchester. He received honorary doctorates from the University of Leipzig and the Institute of Technology Braunschweig. (Even a crater on the moon was named after him in 1979). Wallach was awarded with the Nobel Prize in Chemistry 1910 and learned about it from a newspaper on the train from Hannover to Göttingen.^[15]

3. Wallach's *Annalen* from 1895

The work reported in the *Annalen* paper from 1895 serves as a good example for Wallach's approach.^[1] He describes the bromination of carvone and dihydrocarvone, reports their tri-, tetra-, and penta-

bromides and aims at elucidation of their molecular structure by analyzing chemical and physical properties. Besides the puzzling role Liebig plays in that paper, it contains several other remarkable components (Fig. 2). Concerning conglomerate *versus* racemate crystallization, the most important part is described in the chapter ‘Ueber racemie’ (About racemism). Wallach repeatedly emphasizes the importance of studies on racemism, “*because complete darkness prevails about the principles in which such transformations occur*”; and “*a solution to this question is only expected when numerous suitable examples are studied*”. Wallach compares physical properties, like melting and boiling points as well as crystal shape, of optically active bromocarvones with their inactive modifications (Fig. 2). He particularly points out that he, in contrast to others, believes in the importance of synthesizing optically active as well as inactive crystalline counterparts. Wallach also made a side blow at Emil Fischer, who ignored^[16] Wallach's discussion on racemism ([*My work has*] “*... not received the slightest attention*” Wallach writes in a footnote of ref. [1]).

Wallach clearly points out that there are exceptions from the tendency that ra-

	Bromide aus			
	Carvon, C ₁₀ H ₁₄ O		Bihydrocarvon, C ₁₀ H ₁₅ O	
	<i>activ</i>	<i>r. inactiv</i>	<i>activ</i>	<i>r. inactiv</i>
C ₁₀ H ₁₆ Br ₂ O	flüssig	flüssig	69°–70°	96–97° triklin
C ₁₀ H ₁₆ Br ₃ O	flüssig	74–76° monoklin	88–89° rhombisch hemiëdr.	65° rhombisch
C ₁₀ H ₁₄ Br ₄ O	α	flüssig	flüssig	
	β	120–122° rhombisch hemiëdr.	107–109° monoklin	
C ₁₀ H ₁₅ Br ₅ O	α	142–143° monoklin	124–126°	
	β	86–87°	96–98°	

Fig. 2. Collection of melting points and crystal forms of racemic and enantiopure carvone bromides.

cemates have higher melting points. He states that repeated re-crystallization accompanied with decreasing melting points to conglomerate crystallization (“*come apart into the components*”). In a footnote Wallach mentions that Emil Fischer had doubts that lower-melting racemates are actually true racemates although Wallach had clearly identified such for terpenes.^[17]

As the discussions of Fischer, Wallach and others at that time show, the problem of racemate versus conglomerate was a hot topic. Although 50 years had passed since Pasteur’s optical resolution of tartaric enantiomers, Alfred Werner (1866–1919), for example, only realized in 1899 that conglomerate crystallization could prove his coordination theory.^[18,19]

4. Theodor Liebisch (1852–1922) and Arnold Sommerfeld (1868–1951)

In ref. [1], Wallach lets his colleague Theodore Liebisch finish the paper. Born in Breslau (polish Wroclaw), Liebisch (Fig. 3) received his PhD in geology.^[20] In Berlin he worked at the *Mineralogisches Museum der Friedrich-Wilhelms-Universität*, and became lecturer (Privatdozent) and professor for mineralogy and petrography. During the course of his career he occupied professor positions in Breslau, Greifswald, Königsberg, Göttingen and finally again in Berlin. Liebisch was fellow of the Göttinger and Prussian Academy of Sciences, author of textbooks and monographs and publisher of different mineralogy journals.^[21–25] His work was very much oriented towards physics and optics, in particular, polarization microscopy. Expressions like *Liebisch-twin* and *Liebisch-law* connect his name to different phenomena in mineralogy.^[26] With the exception of some detailed obituaries,^[27–29] not much is known about Liebisch’s personality. However, thanks to Arnold Sommerfeld, assistant of Liebisch in 1893, we have a somewhat closer view on Liebisch. During his time in Göttingen, Sommerfeld was writing almost daily letters to his mother, which are still available.^[30]

Arnold Sommerfeld, one of the founders of modern theoretical physics, also came from Königsberg, where he studied mathematics under Hilbert and Lindemann.^[30] It was actually his affection for mathematics that brought him to Göttingen. Initial contacts to Liebisch, however, were established by the spouses of former Königsberg professors and their network. Sommerfeld’s mother learned indirectly from Adelheid Liebisch that her husband was looking for an assistant. So Sommerfeld was proposed as the candidate to Liebisch. After his positive response,

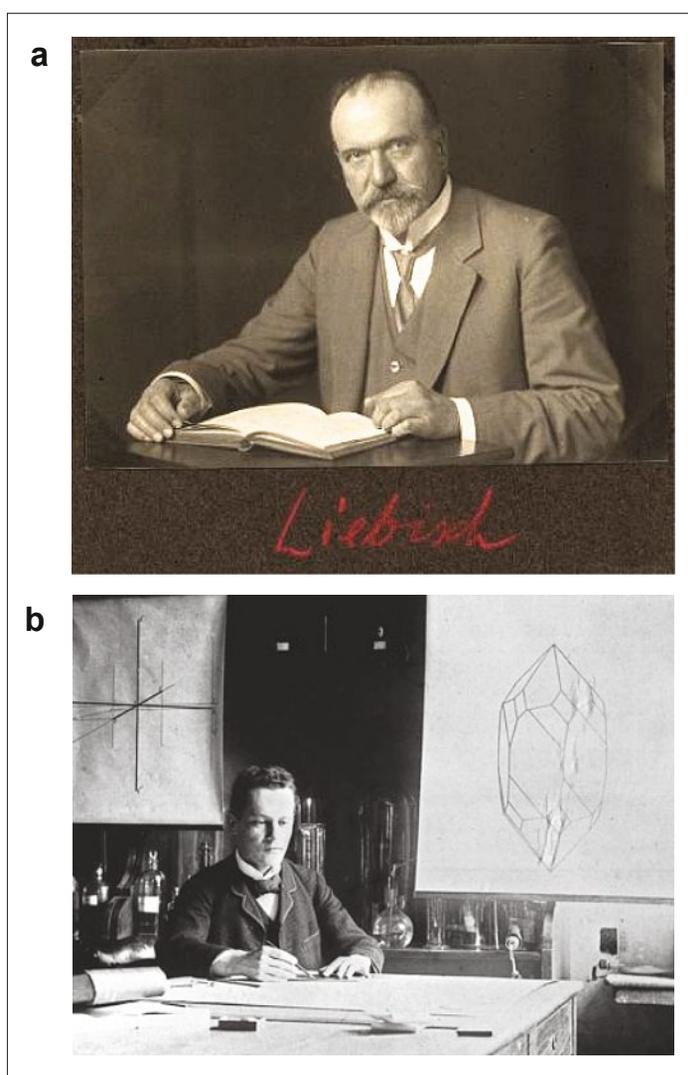


Fig. 3. a) Photograph of Liebisch.

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b) Sommerfeld as post-doc in mineralogy in Göttingen.

From ref. [30].

Sommerfeld accepted the offer and went to Göttingen in 1893 (Fig. 3).

Although now assistant to Liebisch, who requested his full commitment to mineralogy, Sommerfeld had the hope that he would find extra time to pursue mathematics.^[30] Page 141 of the *Annalen* paper actually lists crystallographic characterizations performed by Sommerfeld.

In Göttingen Sommerfeld found a fatherly friend in Wallach. Not only both being from Königsberg, they were also distantly related. Sommerfeld reported about Wallach: “*Always authentic, hard-working, utterly incisive, engaging, helpful*.” and: “*He has an awful lot to do, and is very diligent*.” Interestingly, Sommerfeld cites Wallach commenting on Liebisch: “*Professor Wallach advised me rather against a career such as Professor Liebisch has in mind; Liebisch-style mineralogy in Germany is not, in his opinion, an item much in demand*.”^[30b] (If Wallach was so dismissive about Liebisch-style mineralogy, why did he ask then his colleague for help in the evaluation of his compounds?) Liebisch’s disappointment that Sommerfeld was not committed as he had hoped to miner-

alogy and Sommerfeld’s strong desire for mathematics led finally to the break-up after few months.

5. Density of Racemate Crystals and their Pure Counterparts: Wallach or Liebisch?

Wallach states in the *Annalen* paper that crystal form and *density* of racemic mixtures may differ with respect to their components and the need for evaluation of many samples.^[1] The most important statement in this respect is then: “*I am especially grateful to my highly esteemed colleague professor dr. Th. Liebisch that he allowed the relevant evaluation of material obtained in our laboratory in his mineralogy institute, and that he notably was personally involved. Professor Liebisch discloses the following about the previous results: ...*” (Fig. 4).

By taking then over for the last four pages of the *Annalen* paper, Liebisch makes clear that *he* is the father of the idea of comparing the densities of homochiral crystals with the corresponding racemate

Fig. 4. Crystal analysis: Liebisch reports his results for densities and specific volumes for tartaric acid (a), Wallach's samples (b) and samples Liebisch received from Miers and Pope (c).^[1]

	Dichte	Specificsches Volum	
a Rechtsweinsäure	1,759 ⁹⁶⁾	0,568	
Wasserfreie Traubensäure	1,788 ⁹⁷⁾	0,559	
	Dichte	Specificsches Volum	Contraction in Procenten
b Limonentetrabromid	2,134	0,468	—
Dipententetrabromid	2,225	0,449	2
Carvoxim, activ	1,108	0,902	—
Carvoxim, inactiv	1,126	0,888	1 $\frac{1}{2}$
Fenchonoxim, activ	1,117	0,895	—
Fenchonoxim, inactiv	1,142	0,876	2
β -Isolfenchonoxim, activ	1,134	0,882	—
β -Isolfenchonoxim, inactiv	1,180	0,847	3 $\frac{1}{2}$
Pinakon (?) der Carvonreihe, activ	1,074	0,953	—
Pinakon (?) der Carvonreihe, inactiv	1,095	0,913	4
Carvontetrabromid aus Carvon, activ	2,2428	0,446	—
Carvontetrabromid aus Carvon, inactiv	2,2495	0,444	1 $\frac{1}{6}$
Carvontribromid aus Hydrocarvon, activ	1,958	0,511	—
Carvontribromid aus Hydrocarvon, inactiv	1,958	0,511	—
	Dichte	Specificsches Volum	Contraction in Procenten
c Sobrerol, activ	1,128	0,8867	—
Sobrerol, inactiv	1,131	0,8845	1 $\frac{1}{6}$

crystals of a particular compound: “When I was occupied during summer of 1894 with the production of water-free paratar-taric acid (traubensäure) according to the specifications of A. Scacchi,^[31] I was led to compare the specific volume of these crystals with that of right-handed tartaric acid (Rechts-Weinsäure). It resulted: ...” (Fig. 4a). “It shows that the aggregation of right-handed tartaric acid and left-handed tartaric acid occurs under reduction of volume. The contraction amounts to almost one percent.” “Due to the kindness of Prof. Wallach, I was in the position to perform similar studies on seven racemic compounds and their components synthesized by him. The result is compiled in the following table^{[28];}”^[38] (Fig. 4b). “It shows that only for the last listed body can no change of volume be noted. In all other cases the combination of the optical isomeric bodies into a crystallized racemic compound occurs under contraction. The investigation of Sobrerol (pinolhydrate), that I owe to the gentlemen H. A. Miers and W. J. Pope in London, led to the same result.” (Fig. 4c).

Liebisch also refers (ref. [28] in ref. [1]) to his presentation of these results at the meeting of the Royal Academy of Science in Göttingen on December 8th 1894,^[32] which is confirmed by a list of contributions for the year 1894 (Fig. 5).^[33] Although announced to appear as a report in the proceedings (Nachrichten) of the Royal Academy of Science in Göttingen later, these results were exclusively published in the *Annalen* paper the following year. Remarkably, Liebisch's own list of publications has the last four pages of the *Annalen* paper as his own separate work with the title ‘On density and crystal form

of racemic compounds and their components’.^[28] However, such a subtitle does not exist in the *Annalen* paper.

Wallach seemed clearly annoyed by Emil Fischer's neglect of his earlier work. It seems unlikely that he would allow Liebisch to make the claim of being the initiator of such studies, if Wallach was the initiator himself. Maybe he felt generous by being the sole author? One expects that Wallach and Liebisch must have agreed on the way Liebisch's results went public. In conclusion, we are not able to clearly assign who deserves the credit for the idea of comparative studies of densities. Being at the same university, both probably dis-

cussed the possibility of such experiments. We suggest therefore to turn ‘Wallach's Rule’ into Liebisch-Wallach rule (LWR). In Wallach's elaborate memoirs Liebisch's name appears only once in a plain list of the professors in Göttingen at the time when he arrived. Otherwise, he does not mention Liebisch at all.

The Liebisch-Wallach rule (LWR) describing the tendency that racemates pack denser than their homochiral analogues is purely empirical. LWR has statistically been verified for 65 pairs of resolvable compounds.^[3] However, as the authors noted, there is a statistical bias, because compounds with the racemate profoundly less stable will not be covered. Mandelic acid is a typical example not obeying LWR, the pure enantiomer crystals are denser than those of the racemate.^[7] As Dunitz and Gavezzotti found for 20 chiral-racemic pairs of proteogenic amino acids, LWR does not apply for these compounds either.^[34] Interestingly, a helical intermolecular packing motif, mediated by hydrogen bonds in the homochiral crystal, brings more stability than the centrosymmetric enantiomer packing of the racemate.

A promising approach towards better understanding might be studying well-defined model systems like the two-dimensional (2D) crystallization of chiral molecules at surfaces.^[35] Based on the fact that certain symmetry operations are not available, Lahav and Leiserovitz conjectured that 2D conglomerate crystallization should be favored.^[36] Early studies seemed to confirm this picture, but were likely biased by the choices of surface scientists, who at first focused on amino acids and other polar species.^[37] A newer

a Sitzung vom 8. December 1894.	
F. Klein legt vor: E. Ritter, Ausdehnung des Riemann-Rochschen Satzes auf Formenscharen, die sich bei Umläufen auf einer Riemann'schen Fläche linear substituieren, und A. Sommerfeld, Zur mathematischen Theorie der Beugungserscheinungen. (Gedruckt in den Nachrichten, Mathem.-physik. Kl., S. 328 und 333.)	
W. Voigt: Piëzo- und Pyroelectricität, dielektrische Substanz und Elektrostriction bei Krystallen ohne Symmetriecentrum. (Gedruckt in den Nachrichten, Mathem.-physik. Kl., S. 343.)	
Derselbe legt vor: R. Schütz, Vollständige und allgemeine Lösung des Grundproblems der Potentialtheorie. (Gedruckt in den Nachrichten, Mathem.-physik. Kl., 1895 S.1.)	
Th. Liebisch: Ueber die krystallographischen Eigenschaften racemischer Verbindungen. (Erscheint in den Nachrichten.)	
E. Riecke legt vor: Bachmetjew, Hauptresultate der Untersuchungen über die elektrischen Erdströme in Bulgarien. (Gedruckt in den Nachrichten, Mathem.-physik. Kl., S. 324.)	
b Zur mathematischen Theorie der Beugungserscheinungen.	
Von	
A. Sommerfeld.	
(Vorgelegt von F. Klein in der Sitzung vom 8. December 1894.)	

Fig. 5. a) The list of the presentations in the *Nachrichten* showed that Liebisch talked on Dec. 8th 1894 about ‘On crystallographic properties of racemates’. It states also: ‘Will appear in the Nachrichten.’ At the same meeting Klein presented results of Sommerfeld. b) Sommerfeld published then in the proceedings: ‘About the mathematical theory of diffraction’.

account, however, comes to the conclusion that there is no propensity for either scenario.^[38] Chiral surface crystallization is therefore profoundly different to 3D, where racemate crystals clearly outnumber conglomerates.

In conclusion, although our knowledge about crystallization has made substantial progress during the last two centuries, we realize that – exactly 170 years after Pasteur's seminal publication on conglomerate crystallization of the sodium ammonium salt of *acide racémique*^[39] – not much is understood about the mechanisms governing racemate over conglomerate crystallization.

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- [1] O. Wallach, *Justus Liebigs Ann. Chem.* **1895**, 286, 119.
- [2] Just before this *Annalen* article Wallach published an account on the chemistry of thujone (O. Wallach, *Justus Liebigs Ann. Chem.* **1895**, 286, 90). Newer citations of ref. [1] have often mistakenly both paper's page range (90–143).
- [3] C. P. Brock, W. B. Schweizer, J. D. Dunitz, *J. Am. Chem. Soc.* **1991**, 113, 9811.
- [4] P. A. Levkin, V. Y. Torbeev, D. A. Lenev, R. G. Kostyanovsky, 'Topics in Stereochemistry', Ed. S. E. Denmark, J. S. Siegel, John Wiley & Sons, Inc. **2006**, 25, pp 81–134.
- [5] M. Parschau, R. Fasel, K.-H. Ernst, *Cryst. Growth Des.* **2008**, 8, 1890.
- [6] M. Christmann, *Angew. Chem. Int. Ed.* **2010**, 49, 9580.
- [7] J. Marciniak, M. Andrzejewski, W. Cai, A. Katrusiak, *J. Phys. Chem. C* **2014**, 118, 4309.
- [8] T. Friščić, L. Fabian, J. C. Burley, D. G. Reid, M. J. Duer, W. Jones, *Chem. Commun.* **2008**, 1644.
- [9] K.-H. Ernst, *Isr. J. Chem.* **2017**, 57, 24.
- [10] W. S. Partridge, E. R. Schierz, *J. Chem. Educ.* **1947**, 24, 106.
- [11] 'Otto Wallach 1847–1931. Chemiker und Nobelpreisträger, Lebenserinnerungen: Potsdam, Berlin, Bonn, Göttingen', published and annotated by G. Beer, H. Remane, Verlag für Wissenschafts- und Regionalgeschichte, Berlin, **2000**.
- [12] L. Ružička, *J. Chem. Soc.* **1932**, 1582.
- [13] Lecture before the German Chemical Society, **1891**, from ref. [12].
- [14] O. Wallach, *Justus Liebigs Ann. Chem.* **1888**, 246, 221–239.
- [15] "Als ich mir in Hannover eine Abendzeitung gekauft hatte und darin auf dem letzten Weg nach Göttingen las, fand ich die mir unglaubliche Notiz, dass mir der Nobelpreis für 1910 verliehen sei. Zu Haus empfing mich das bestätigende Telegramm aus Stockholm. Ein offizieller Brief von dem Sekretär der Schwedischen Akademie, Aurivillius und ein Privatbrief von Arrhenius brachten weitere Bestätigung." ("When I bought an evening paper in Hannover and read it on the last step of the journey to Göttingen I found the unbelievable report that I had been awarded the Nobel Prize for 1910. At home I received the confirmatory telegram from Stockholm. An official letter from the secretary of the Swedish Academy, Aurivillius, and a private letter from Arrhenius brought further confirmation.") from refs [6] and [11].
- [16] E. Fischer, *Ber. Dtsch. Chem. Ges.* **1894**, 27, 3189.
- [17] O. Wallach, *Ber. Dtsch. Chem. Ges.* **1891**, 24, 1525.
- [18] K.-H. Ernst, F. R. W. P. Wild, O. Blacque, H. Berke, *Angew. Chem. Int. Ed.* **2011**, 50, 10780.
- [19] A. Werner, A. Vilmos, *Z. Anorg. Chem.* **1899**, 21, 145.
- [20] T. Liebisch, 'Über die in Form von Diluvialgeschieben in Schlesien vorkommenden massigen nordischen Gesteine', Phil. Diss., Breslau, **1874**.
- [21] T. Liebisch, 'Physikalische Krystallographie', Veit & Comp., Leipzig **1891**.
- [22] T. Liebisch, 'Grundriss der Physikalische Krystallographie', Veit & Comp., Leipzig **1896**.
- [23] T. Liebisch, 'Die Synthese der Mineralien und Gesteine', Festschrift im Namen der Georg-Augusts-Universität zur akademischen Preisverleihung am V. Juni MCCCXI. Dieterich, Göttingen, **1901**.
- [24] T. Liebisch, A. Schönflies, O. Mügge, 'Krystallographie, Encyclopädie der mathematischen Wissenschaften mit Einschluß ihrer Anwendungen', Teubner, Leipzig, **1905**.
- [25] K. Liebisch, 'Geometrische Krystallographie', W. Engelmann, Leipzig, **1881**.
- [26] G. Gross, *Schweiz. Mineral. Petrogr. Mitt. (Bull. Suisse Minéral. Pétrogr.)* **1972**, 52, 523.
- [27] K. Schulz, *Centralbl. Mineral. Geol. Paläol.* **1922**, 417.
- [28] O. Mügge, *Nachr. Ges. Wiss. Göttingen. Geschäftliche Mitt.* **1922**, 1, 79.
- [29] A. Johnsen, *Sitzungsber. Preuss. Akad. Wiss.* **1923**, CXIII–CXV.
- [30] a) M. Eckert, 'Arnold Sommerfeld, Atomphysiker und Kulturbote 1868–1951. Eine Biografie', Wallstein, Göttingen, **2013**; b) M. Eckert, 'Arnold Sommerfeld: Science, Life and Turbulent Times 1868 – 1951', Springer, New York, **2013**.
- [31] A. Scacchi, *Atti R. Accad. delle Sc. Fis. e Mat.*, **1869**, 4, 4. 24 p. 1 Tav. Napoli.
- [32] T. Liebisch, Mitgeteilt in der Sitzung der [communicated in the meeting of the] Königl. Gesellschaft der Wissenschaften zu Göttingen, 8. December, **1894**.
- [33] *Nachr. Ges. Wiss. Göttingen. Geschäftliche Mitt.* **1895** (1), p. 13.
- [34] J. D. Dunitz, A. Gavezzotti, *J. Phys. Chem. B* **2012**, 116, 6740.
- [35] K.-H. Ernst, *Phys. Status Solidi B* **2012**, 249, 2057.
- [36] M. Lahav, L. Leiserowitz, *Angew. Chem.* **1999**, 111, 2691.
- [37] S. M. Barlow, R. Raval, *Surf. Sci. Rep.* **2003**, 50, 201.
- [38] S. Dutta, A. J. Gellman, *Chem. Soc. Rev.* **2017**, 46, 7787.
- [39] L. Pasteur, *Ann. Phys.* **1848**, 24, 442.