Abstract. The Norwegian physicist Lars Vegard studied with William H. Bragg in Leeds and then with Wilhelm Wien in Würzburg. There, in 1912, he heard a lecture by Max Laue describing the first X-ray diffraction experiments and took accurate notes which he promptly sent to Bragg. Although now remembered mainly for his work on the physics of the aurora borealis, Vegard also did important pioneering work in three areas of crystallography. He derived chemical insight from series of related crystal structures that he determined, Vegard's Law relates the unit cell dimensions of mixed crystals to those of the pure components, and he determined some of the first crystal structures of gases solidified at cryogenic temperatures.

Contents

1. Introduction

Following the proposal of Max von Laue that X-rays could undergo diffraction by a crystal, Walter Friedrich and Paul Knipping carried out the first X-ray diffraction experiment in Munich in April 1912. While enjoying an early summer English seaside holiday in the same year William Henry Bragg (WHB) and his son William Lawrence Bragg (WLB) were discussing its implications. Even in the era of the Internet this would be considered rapid dissemination of results. That it happened a century ago was due to Lars Vegard, a young Norwegian who was in the right place at the right time with the necessary contacts and interests. The all-important letter that Vegard wrote to WHB informing him of Laue's work has been described on the Nobel Prize website and by John Jenkin in his biography of the Braggs (1a,b). This letter is reproduced in a comprehensively documented book by A. Authier

which has recently appeared under the auspices of the International Union of Crystallography (1c). Today Vegard is principally remembered for carrying out some of the most important investigations into the physics of the aurora borealis. A comprehensive summary of this research and insights into his life (in Norwegian) have been contributed by Alv Egeland (2). A valuable feature of this work is a table on the final 12 pages listing all of Vegard's scientific publications. Most of these are written in fluent English or German. Vegard developed an early interest in X-ray spectroscopy, the results of which during 1916-1920 he applied to the quantum theory of the atom then under development. A fascinating account by Helge Kragh (3) describes how a plausible correlation between the frequencies of characteristic X-radiation of the elements and their atomic number misled Vegard and other leading physicists into believing that 3 electrons occupied the innermost ring or shell. However, Vegard also carried out important pioneering work in X-ray crystallography. Vegard's life and crystallographic research have been the subject of a 160-page book in Norwegian by Egeland, Pedersen & Torstveit (4). The main objective of this Historical Review is to provide the English-speaking reader with a critical evaluation of Vegard's crystallographic work based on his published papers. For convenience his mature crystallographic research is presented below in three sections (**3**, **4** and **5**), but it should be appreciated that in all these areas a major factor in his success was his ability to derive conclusions relevant to both physics and chemistry from his experiments, allied to his engineering skill with apparatus.

2. Early life, education and first scientific work

Egeland's article(2) provides much information about this period of Lars Vegard's life. Born in 1880 and christened Lars Nilsen (the son of Nils), he was the seventh child of farmer Nils Gundersen and his wife Anne Gundesdatter, who lived in the district of Vegarshei. His father's early death in 1886 might have been expected to extinguish any educational opportunity for this farm boy. However, his parents were people of some importance: Nils Gundersen had served in local government, and Anne Gundesdatter's family were described as "well-to-do" (2). While the eldest brother took over the farm, thanks to his own strong will and encouragement from his family Lars was able to get a good education, culminating in a physics degree from the University of Kristiania (now Oslo) in 1905. Around 1900 he changed his surname to "Vegard Nilsen" , referring to his home district; and subsequently he dropped the "Nilsen".

A leading member of the faculty of physics at Kristiania was Kristian Birkeland, a celebrated auroral researcher. Although it was disputed at the time, Birkeland correctly postulated that the impact of electrons ejected by the sun upon gas in the upper atmosphere produced the aurora. Furthermore, he constructed a device, the "terrella", in which a magnetised sphere suspended in a partial vacuum and bombarded with cathode rays (electrons) elicited an aurora-like glow near its poles. Birkeland was independently wealthy. Following the example of Lord Kelvin, he carried out applied research to earn the money needed to support his basic research. Putting his knowledge of plasma physics to practical use, the Birkeland-Eyde process used hydroelectric power, available in abundance in Norway, to fix atmospheric nitrogen. The product, Norgessalpeter (calcium nitrate) was in demand as a fertiliser. Birkeland used his own funds to employ a number of promising students as his assistants, including Vegard starting in 1906. The next year, with his support, Vegard obtained a government stipend that enabled him to study abroad. Characteristically, he opted for

the most prestigious placement possible: the University of Cambridge, in the laboratory of J. J. Thomson, who had received the Nobel Prize in 1906 for his research on the conduction of electricity by gases. This topic had obvious relevance to the interests of Birkeland and Vegard. However, Vegard's first publication while at Cambridge reported on investigations of osmotic properties (5). This broadening of his scientific interests may have made him receptive to the blandishments of William Henry Bragg.

2.1. *First contact with William Henry Bragg and X-rays*

After his appointment as Professor of Physics at the University of Leeds, WHB visited Cambridge to recruit promising young researchers. As one of his first employees, Vegard joined him in January 1909 (6) and began a careful study of the polarisation of X-rays. This phenomenon had already been reported by WHB's sometime intellectual adversary Charles Glover Barkla (7a), who proposed an understandable explanation in terms of "ether pulses", i.e. waves. Barkla's experiment deserves recognition as a landmark of physics (7b). However, at this time WHB was firmly wedded to the concept that X-rays were corpuscular in nature. Vegard's main contribution was to carry out experimental work with great attention to compensation of possible errors. A collimated primary beam of X-rays was directed head-on at a "secondary radiator", a long cylinder of paraffin which tapered to a cone with apex at the aiming point of the X-rays. Secondary radiation emitted by the paraffin was detected by paired electroscopes on either side of a containment box which could be turned through 90°, thus compensating for any failure to centre the most intense part of the beam exactly on the tip of the cone. The electron beam exciting the primary X-rays was maintained in a constant horizontal orientation, but the angle at which it struck the anode could be varied by turning the anode about a horizontal axis perpendicular to this electron beam. Vegard found a small but regular variation of the polarisation with this angle. This work led to the publication in March 1910 of a paper (8) in *Proceedings of the Royal Society* with the sole authorship of "Mr. L. Vegard", communicated by Prof. W. H. Bragg F.R.S. The Edwardian era is generally considered to be hierarchical, but *Proc. Roy. Soc.* appears to have been unexpectedly democratic: of the 8 papers in this issue, 4 had authors with the title "Mr". Before explaining the observations in terms of WHB's "neutral pair" theory Vegard's paper includes the sentence "Sir J. J. Thomson has tried to make the ether pulse theory consistent with observations by introducing new properties for the pulse-medium, and assumes that the ether has a structure, and that the energy radiating from the pulse centre is transmitted along 'lines of force' with undiminished intensity". One can only wonder if asserting gentle disagreement with his previous mentor caused Vegard any discomfort.

2.2. *PhD research in Würzburg and contact with Laue*

Returning to Oslo in 1910 with an emerging publication record but no doctorate (at this time the PhD degree was awarded by universities in Germany, Scandinavia and the United States but not in the United Kingdom), Vegard was appointed to a lectureship. Here he resumed his research on the aurora. Extending Birkeland's idea of electron impact on the upper atmosphere, he assumed that to preserve neutrality, positive ions from the sun were also arriving (2). His ultimately successful search for the faint positive-ion aurora occupied him for many years. In 1911 Vegard obtained another scholarship, which once again he used to work in a prestigious laboratory. This time he went to Würzburg to work with Nobel laureate Wilhelm Wien and develop these ideas. This research (3), mainly on discharges in gases and canal rays (positive ions), provided enough material

for his PhD and led to a long paper in *Annalen der Physik* (9). It was during this time in Würzburg that he heard Laue's lecture about the X-ray diffraction experiments carried out two months earlier in Munich. With his freshly minted knowledge about X-rays he immediately appreciated their importance and wrote a letter to WHB that has been described as "containing precise and detailed information" (1a).

3. Pioneering structure determinations and later extensions

Vegard's earliest crystallographic publications appeared in 1916 and 1917. His citizenship and residence in neutral Norway during World War I must have been an advantage, as he was able to publish both in *Philosophical Magazine* and in *Physikalische Zeitschrift*. Vegard's methods for collecting and interpreting data closely followed those of the Braggs, and his earliest studies were cautious. His structure determinations of silver (10), gold and lead (11) confirmed the expectations that they would have a similar space-lattice to the one for copper already published by the Braggs (12). However, he soon showed boldness in his choice of structures to determine, including the earliest ones in a tetragonal space group (11). He attempted significant applications to chemistry, unfortunately exceeding the capabilities of the methodology. Thus he sought to determine whether zircon (11) should be properly characterised as $Zr(SiO_4)$ or $(ZrO_2)(SiO_2)$, and he compared the structures of ammonium iodide and tetramethylammonium iodide (13a). From such structural information he tried to draw conclusions about the sizes of atoms.

Although his first paper in his series in *Philosophical Magazine* (10) acknowledges the Braggs "for valuable information with regard to the methods of the crystal analysis", at times communication was imperfect. Thus his second paper in this series (11) includes a paragraph starting "Not being aware of the fact that the Spinel group recently has been analysed by W. H. Bragg, I have also made an analysis of the structure of this group" ... and finishing "so a more detailed account will be superfluous."

3.1 Apparatus and procedures

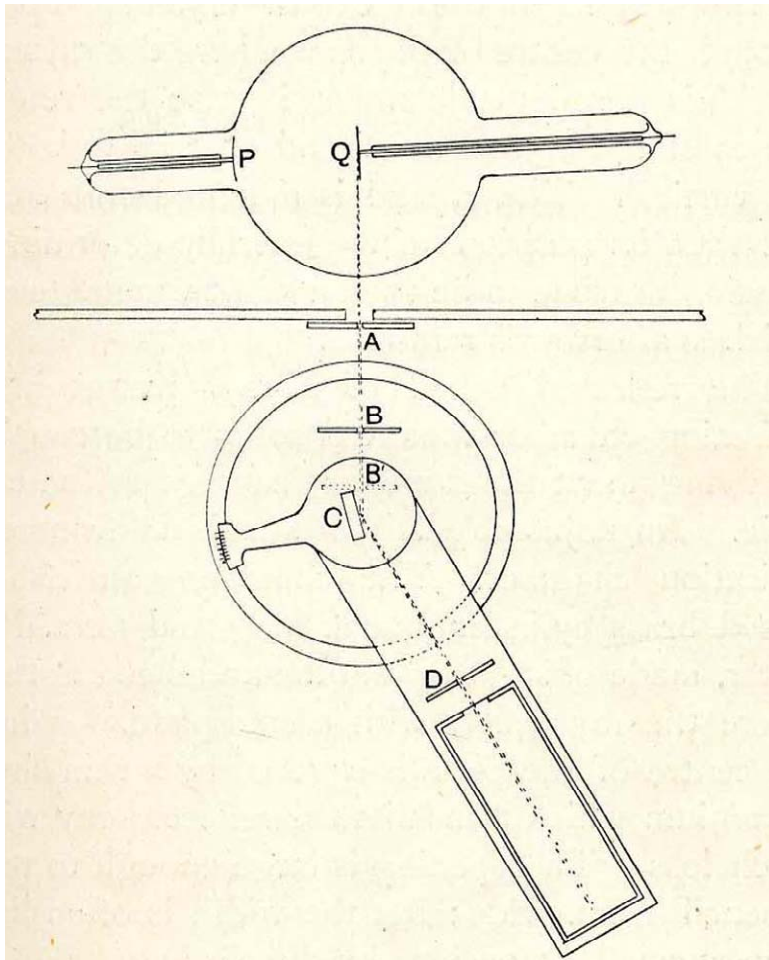It is important for the modern reader to realise just how difficult it was to obtain data at this time.

Figure 1. Diagram of Bragg's spectrometer dating from 1913 (14)

Vegard made WHB's spectrometer (Figure 1; 14) somewhat easier to operate by mounting it on an optical goniometer (10) with the collimated light source for the optical goniometer parallel to the X-ray beam and the telescope parallel to the axis of the ionisation chamber. The specimen crystal was mounted onto the crystal table with wax; and, by using the optical goniometer, a prominent face was accurately aligned in what would become the reflecting orientation. A height adjustment screw underneath the table enabled the oriented crystal to be raised to a position coincident with the X-ray beam. As many orders of diffraction as possible were measured, typically from 1 to 3, 4 or 5. For additional measurements to be made, a different face, which might be from an entirely different specimen crystal, had to be placed in reflecting position. Thus the scaling between different orders of diffraction followed a trend that was understood in general terms (11), but the scaling between reflections from different faces could be completely arbitrary.

The X-ray "bulbs" (tubes) he used at this time relied on the ionisation of residual gas elicited by the high voltage from an induction coil. Ions moving towards the electrodes cause a cascade of ionisation; electrons arising in this process strike the anti-cathode (rhodium in Vegard's early work), causing it to emit X-rays. The gas pressure had to be carefully controlled or the tube would self-destruct. Detection of diffracted X-rays was with an ionisation chamber following WHB's design. To make sure that no orders of diffraction were missed, an initial scan of the entire ionisation curve was

carried out with fairly wide (1 mm) slits. Each maximum attributable to the strongest Rh line was then re-scanned with a narrower (≈0.4 mm) slit.

Because the overall efficiency of the apparatus was low, the specimen crystals had to be very large as well as faceted. In his study of gold (11) Vegard reported that "one specimen had the form of an octahedron, but as it had linear dimensions of the order of only one millimetre, we did not with our instrument detect any reflexion from it". His report on tetramethylammonium iodide (12) includes the statement that "crystals ... were quite small (greatest linear extension about 5-6 mm)". His research benefited from the availability of large high-quality specimens in the excellent Mineralogical Museum at his university, initially in the same building as his laboratory. He expresses his thanks (11) for the loan of specimens, including precious ones like gold.

Notwithstanding the errors introduced by strong absorption and extinction along with broad maxima from differently sized specimen crystals, the data thus obtained were sufficient to determine the lattice and provide a reasonably exact value of the cell dimensions. However, as will be seen, the determination from intensity data of parameters governing the placement of lighter atoms within the unit cell has been liable to error. In fact, Vegard contributed a significant improvement to our understanding of factors affecting intensity (11).   First he stated that "...the distribution of intensities... has been treated by W. H. and W. L. Bragg. The calculation is based on the assumption that the amplitude reflected from a certain point-plane is proportional to the mass associated with unit area of the plane. In view of the theory of secondary radiation given by Sir J. J. Thomson (15), it would be more natural to suppose the amplitude proportional to the *number of electrons* per unit area... and we should put the reflecting power of an atom proportional to the atomic number."

3.2 Some significant early studies

The first subject in Vegard's series of X-ray crystallographic papers was the structure of silver (10). It should be noted that, as WLB had done before (16), he defined the length of each unit cell edge as *2a* but referred the indices of planes to *a*. The spacings d_{100}, d_{110} and d_{111} were calculated from Bragg's Law, and the ratios d_{110} / d_{100} and d_{111} / d_{100} were found to match those derived by the Braggs for a face-centred cubic lattice (17). An appropriate value for the number of atoms per unit cell was obtained from the measured density and the calculated volume. The second paper (11) was more ambitious: not only were Au and Pb shown also to have face-centred cubic structures, but the majority of the paper was devoted to the structure of zircon with some measurements also on the tetragonal rutile and cassiterite. These latter structures were erroneously postulated to be isomorphous with zircon by the substitution of Ti or Sn at both the Zr and the Si sites. By consideration of d_{100} and d_{001} spacings and the intensity distribution for the various orders of diffraction Vegard concluded that the Zr and Si atoms were arranged on a diamond lattice. The locations of O atoms, which did not occupy special positions, had to be related to parameters which were determined by algebraic calculations of structure factors. In hindsight it is obvious that the available data were insufficient to determine the parameters correctly, and the proposed structure with 2-coordinate Zr and Si atoms was incorrect. A third publication in 1916 (18) applied similar procedures to the structures of xenotime (YPO_4) and the anatase form of TiO_2. The most "chemical" study of this period (13a) compared $NH_4^+I^-$ with $N(CH_3)_4^+I^-$. In the former cubic structure the I and N atoms were supposed to have face-centred cubic lattices similar to those for Na and Cl in rock salt.

In the latter tetragonal structure a lattice of I and N atoms was proposed, with tetrahedral groups of carbon atoms on their own sites separated from the N atoms (Figure 2). For comparison a drawing of the structure from a modern redetermination (13b) of $N(CH_3)_4^+I^-$ is shown in Figure 3. Here the nitrogen atoms, correctly located within the carbon tetrahedra, are placed on the unit cell origin and equivalent positions.
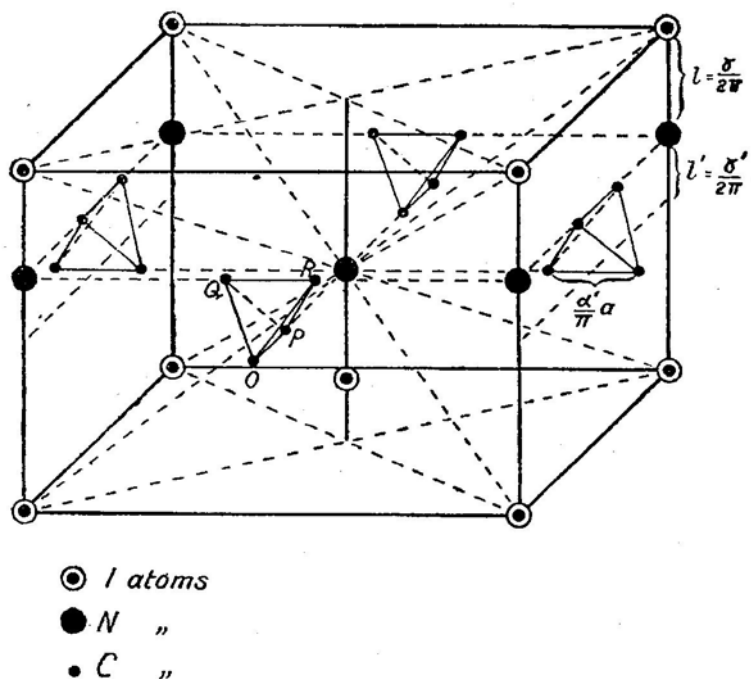

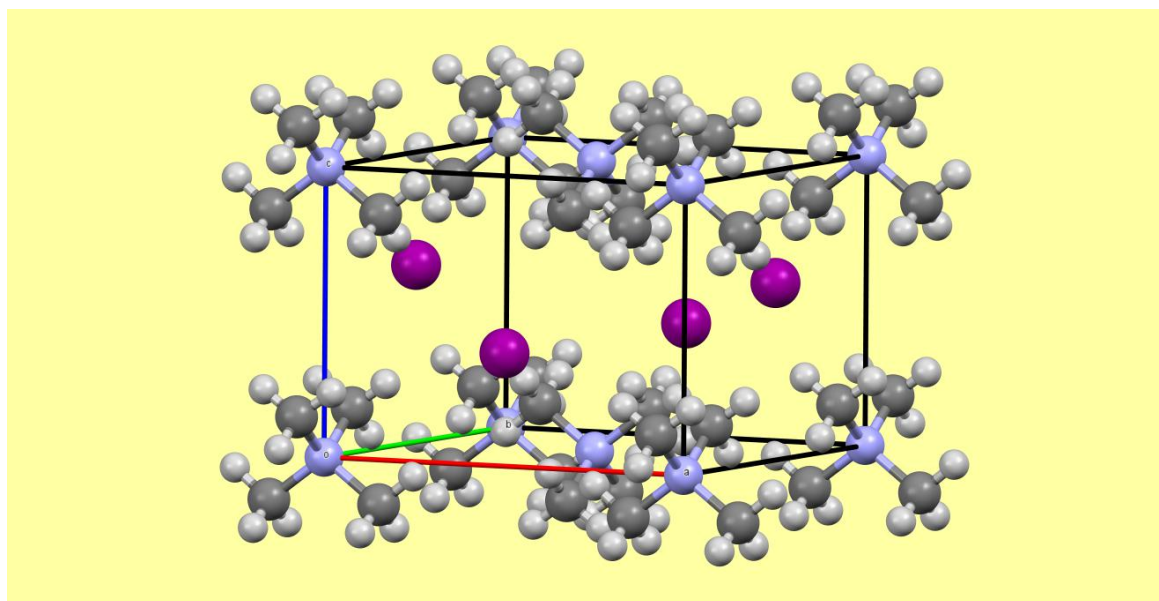Figure 2. The structure of tetramethylammonium iodide as published by Vegard in 1917 (13a)

Figure 3. Drawing prepared with Mercury of the structure of tetramethylammonium iodide from a modern redetermination (13b)

3.3 Redeterminations

For subsequent studies Vegard switched to the Debye-Scherrer powder diffraction method for data collection, thus eliminating the need for large crystals and providing the ability to measure *all* reflections up to a specified maximum deflection angle. However, indexing the pattern was a challenge. Vegard seems to have had a natural talent for this. For instance, the entry in the compendium of "Standard X-Ray Diffraction Patterns" (19) for strontium nitrate states that "The first, by Vegard (20) in 1922, was well indexed and misses few lines, although it is of less precision than the later patterns."

Using this technique, he revisited the structures of anatase, zircon, rutile and cassiterite (21). While his earlier structure of anatase was largely confirmed, he had to change the location of oxygen atoms in zircon, creating the now well-known SiO_4 tetrahedra but also associating the O atoms with Zr. The structures of rutile and cassiterite were shown to differ from that of zircon. Assuming that the structures are completely ionic, he calculated atomic radii (which will be compared with modern values of crystal ionic radii (22) given in parentheses). From the structure of anatase he obtained 1.24 (1.26) Å for O and 0.63 (0.745) Å for Ti; from zircon, 1.18 (1.26) Å for O, 0.99 (0.86) Å for Zr, 0.49 (0.54) Å for Si. Independent redeterminations of the structure of zircon by several authors appeared in 1926 and 1927. Working in WLB's laboratory, Binks (23) acquired data both with the ionisation spectrometer and from Debye-Scherrer photographs . The results agreed with Vegard's assignment of the lattice and overall arrangement of oxygen atoms, though with detailed differences in parameters governing the O atom positions.

In the following year Vegard reported the structure of xenotime (24), YPO_4. His original structure (18) showed a close analogy with that of zircon and led to a "constitution formula" of YO_2PO_2, but in an addendum to the next year's paper on $NH_4^+I^-$ and $N(CH_3)_4^+I^-$ (12) that discussed xenotime he wisely concluded that "The ordinary chemical constitution formula is intimately related to the idea of a molecule; but in the crystalline state the idea of a molecule as an individual system has lost its significance." Once the zircon structure had been corrected (21), any lingering worries about PO_2 units disappeared, and the combination of three-valent Y and five-valent P in xenotime could be seen to play the same role as four-valent Zr and Si in zircon. The similarity of atomic sizes between some rare earth elements and Y led to the conclusion that they could occupy some of the Y sites in the lattice and explained why natural samples of xenotime usually contain such impurities.

Also in 1927, with his student Karl Sollesnes as co-author, Vegard reported (25) a redetermination of the structure of tetramethylammonium iodide along with new determinations of the chloride and bromide salts. The latter two salts were too hygroscopic for data collection when fully exposed to the atmosphere, but enclosure of the samples in a capillary made it feasible to use the Debye-Scherrer method. With some understatement the paper states that "certain changes of the parameters had to be made". Specifically, the nitrogen atoms had to be moved by *a*/2 to place them in the centres of the previously empty carbon tetrahedra with N-C distances about 1.5 Å. With less domination by the halide ion, the chloride salt in particular enabled the N and C atoms to be positioned with reasonable accuracy and structural units of $N(CH_3)_4^+$ to be correctly inferred. The assumption that atoms were in contact enabled the ionic radii of Cl^-, Br^- and I^- to be estimated as 1.82 (1.67), 1.96 (1.82) and 2.15 (2.06) Å [modern values (22) once again in parentheses]. The

modest over-estimate of the size of halide ions led to an under-estimate of the van der Waals radius of hydrogen; even so, Vegard and Sollesnes seemed surprised that their value of 0.85 Å was so big.

4. Mixed crystals and Vegard's Law

Those crystallographers who remember Vegard's name are most likely to associate it with the Law named after him. Already in 1917 Vegard and Schjelderup applied X-ray diffraction to elucidate the nature of mixed crystals (26) where the pure components had modest differences in their unit cell dimensions. Before the advent of X-ray diffraction there seemed to be no way to discriminate between the hypotheses that mixed crystals were formed of (i) thin homogeneous layers of the two pure components, (ii) orderly alternation of component atoms within the same lattice, or (iii) random substitution within a common lattice. Careful searches (26) with the ionisation spectrometer for diffracted X-ray beams from mixed crystals of KBr : KCl in proportions of 3 : 97, 50 : 50 and 89 : 11 mol % and KBr : NH_4Br 67.5 : 32.5% did not show doubled maxima as expected for the superposition of patterns in case (i), nor new peaks from a new unit cell as expected for (ii) particularly in the 50:50 mixture, and led to the conclusion that substitution was random. To banish any worries that these searches might have missed the extra peaks from orderly substitution, mixtures of cubic KCl : KBr, cubic KCl : NH_4Cl and rhombic K_2SO_4 : $(NH_4)_2SO_4$ were subsequently examined by the Debye-Scherrer method (27). All observed maxima could be indexed in a unit cell that was a compromise between the unit cells of the pure components.

Furthermore, the additivity law now known as Vegard's Law was formulated, initially for the KBr : KCl system. For a mixture with p mol % of KCl the unit cell edge

$$a_m = [(100-p)/100]\, a_{KBr} + (p/100)\, a_{KCl}.$$

Since pure NH_4Cl has a different unit cell than KCl : NH_4Cl mixtures, the additivity law could not be verified directly for such a system. However, a hypothetical a_{NH4Cl} could be calculated by extrapolation. This hypothetical cell was less dense than the actual cell for pure NH_4Cl. In this paper (27) Vegard introduced the concept of "Mikrozerstörung (microdestruction)" at sites where an inappropriately sized atom had been forced into the lattice. Since the lines observed with the mixed crystals were as sharp as those from powders of the pure components, and the decrease of intensity at higher diffraction angles was no faster, microdestruction cannot have been significant in the systems that were examined. The conclusion was that, to a limited extent, atoms could adjust their size to fit their environment. Always calling it "the additivity law", Vegard was well aware that it was the type of law that only applied to a limited range of substances and was an excellent approximation rather than an exact equation.   In a later paper (28) Vegard and Dale broadened the range of systems examined to include alloys as well as salts. Their mixtures behaved in various ways. Mixtures of $Pb(NO_3)_2$: $Ba(NO_3)_2$, which have a 3.4% difference in cell lengths of the pure components, gave near-perfect agreement with the additivity law: the correlation coefficient between cell length and mol % $Pb(NO_3)_2$ was -0.999 . In the case of NaBr : NH_4Br, where the difference in size between cations was greater and the pure substances adopted different crystal forms, no atom substitution could be detected. Mixtures of Cu:Ni exhibited excellent agreement, while only limited replacement was possible with Cu-Co, in which Cu tolerates up to 13% of Co atoms while Co tolerates up to 8% Cu. This last result came as a surprise. The atomic dimensions of

Ni and Co are similar, and both were known to crystallise in a cubic form; yet they differ in their behaviour with Cu. Vegard and Dale suggested that the other known form of Co, hexagonal, was the stable form of truly pure Co, and crystallisation of the cubic form of Co was induced by small quantities of impurities. Finally, they devoted considerable attention to reinvestigation of the Au : Cu system, which has a 12% discrepancy in cell lengths.. While Kirchner (29) and Lange (30) had found excellent adherence to the additivity law, Bain (31) had found large deviations. The experiments of Vegard and Dale confirmed the validity of the additivity law for their mixtures, which had been crystallised by rapid cooling. They attributed Bain's divergent results to intermetallic compound formation permitted by slower cooling, finding lines among Bain's data that could be matched to AuCu. A plot of Vegard's data for Au : Cu shows a small systematic deviation from linearity, but the correlation coefficient between cell length and mol % Au still has the impressive value of 0.997 .

Decades before grinding the components together with or without a drop of solvent became popular as a way to prepare co-crystals, Vegard applied this technique to the preparation of mixed crystals. First, the product of grinding KCl and KBr together gave the same X-ray diffraction peaks already measured from the corresponding mixed crystals. By contrast, simply shaking together previously powdered KCl and KBr led to a superposition of peaks from both pure compounds (32). A subsequent study (33) confirmed formation of mixed crystals from the KCl/KBr system even under careful exclusion of moisture, and from HgCl/HgBr as well, but not from Au/Cu.

5. Low-temperature crystallography

One of Vegard's most original contributions to the development of crystallography was based on a misconception. In the early 1920s a green line in the auroral spectrum at 5577 Å defied conventional explanation. Knowing that within the troposphere the air temperature decreased with height, he incorrectly but plausibly assumed that this trend continued at higher altitudes, to the point that minute crystals of nitrogen might form. Such crystals could (and do) display different spectral characteristics than gaseous nitrogen (3,34). Following his usual style, in order to investigate the spectroscopic and structural properties of solidified gases, he went to work in the world's foremost cryogenics laboratory, that of the Dutch Nobel laureate Heike Kamerlingh Onnes in Leiden. This work is summarised in a paper (35) which cites a number of earlier papers. Subsequently Vegard established his own low-temperature laboratory in Oslo. An improved version of his apparatus dating from 1931 is shown in Figure 4 (36). Equipment was available to him for making liquid air and liquid hydrogen, to be used as refrigerants. His design of the apparatus for X-ray data collection kept the refrigerant in vacuum-jacketed chamber A separate from the crystallizing sample in camera B. A thick copper cylinder 1 chilled by the refrigerant conducted heat away from a copper spike 2 embedded in it. The gas sample admitted to the camera would freeze into a polycrystalline mass on the spike. Irradiated with X-rays from the tube C, the sample yielded a powder diffraction pattern which could be recorded by the Debye-Scherrer technique. Although a connection between solid nitrogen and the aurora was subsequently disproved (37), once Vegard had made the intellectual effort and capital investment to develop this technique, he carried on his cryogenic investigations to a wide range of small molecules: α-N_2 (38), β-N_2 (39), CO (40), α-O_2(41), β-O_2 (42), γ-O_2 (42), H_2S (43), H_2Se (43), COS (44) and N_2O_4 (36).

Die neue Kamera mit ihrem Anschluß an den Kühlapparat und das Röntgenrohr ist in Fig. 1 abgebildet. Die Konstruktion des neuen Röntgenrohrs ist in Fig. 2 gegeben.

In Fig. 1 bedeutet A den unteren Teil des Kühlgefäßes, B die Röntgenkamera, C einen Teil des Röntgenrohrs, der den Strahlengang von der Antikathode angibt.

Fig. 1.
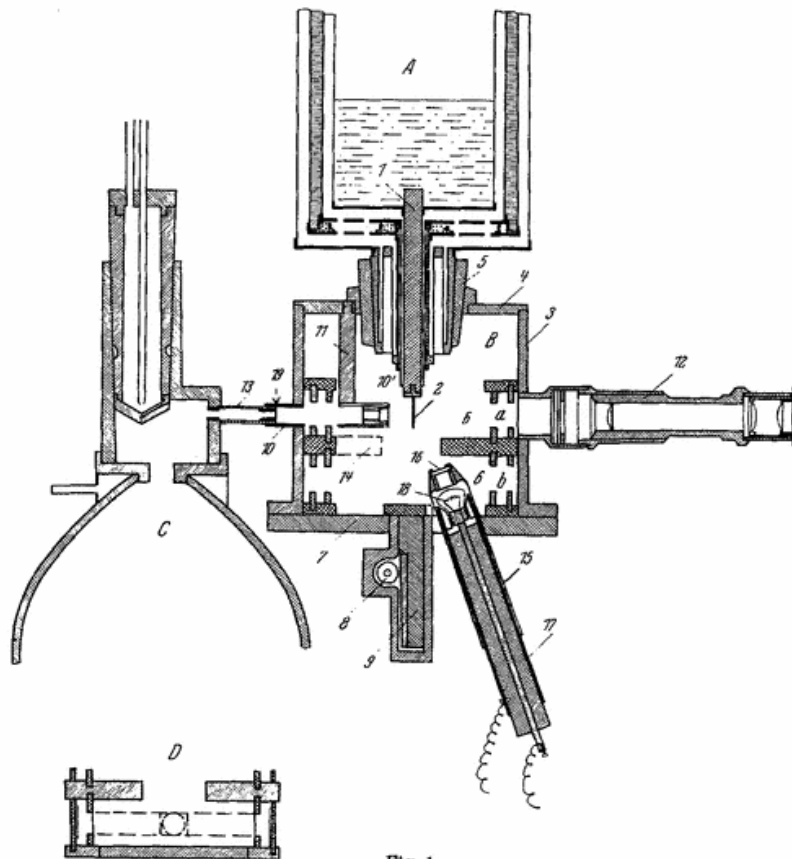
Das Kühlgefäß A ist in einer früheren Abhandlung beschrieben*, hier ist nur der untere Teil gezeichnet, um den Anschluß an die Kamera anzugeben. Der dicke Kupferstab (1), dessen oberes Ende in die Kühlflüssigkeit hineinragt, trägt unten ein ungefähr 1 mm dickes und 15 mm

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* L. Vegard, Det Norske Vid. Akad. Skr. 1, Nr. 8, 1930.

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Figure 4. Diagram of Vegard's low-temperature apparatus (36)

5.1. *Limitations of Vegard's apparatus and ways he surmounted them*

This success could only be achieved by working around the limitations of the apparatus. Diffraction from the copper spike would obscure some maxima from the sample, but repeating the experiment with a silver spike relocated the interfering maxima so that, by combining data from the two experiments, all diffraction maxima from the sample could be recorded (42). Another problem involved the measurement and control of the sample temperature. Although the temperature of the copper cylinder could be and was measured, and electric heating could be applied if a higher temperature than that of the refrigerant was needed, it was only an assumption that the temperature of the spike did not differ appreciably from that of the cylinder. This impaired Vegard's first study of solid oxygen. Oxygen has three solid modifications: α below 24 K, β between 24 and 44 K and γ between 44 K and the melting point of 54 K. The first diffraction pattern from what he thought to be α-O_2 was subsequently found to be identical with that from β-O_2(42). Since the boiling point of the liquid hydrogen refrigerant is 20.3 K (45), the spike should have been just cold enough to freeze out α-O_2, but evidently there was too much heat leakage. Subsequently Vegard did succeed in determining this structure (41) along with the β and γ forms (42). With its narrow range of thermal stability the successful crystallization and determination of the γ form was a particular triumph. Vegard also succeeded with the even more difficult task of determining the structure of β-CO, which is only stable between the transition temperature of 61.5 K and the melting point of 68.2 K (40). The temperature of the copper cylinder alone was not a good enough guide, but Vegard had access to accurate vapour pressure data (46) for CO. Its great temperature sensitivity, ranging from 25.2 mm Hg at the transition point to 117 mm Hg at the melting point, allows an accurate calculation of the temperature of the sample. Regulating the pressure to 60 mm Hg ensured a temperature around 65 K.

Vegard successfully integrated structural studies of simple molecules at low temperature with spectroscopic observations after irradiation

under similar conditions. His results on nitrogen were of particular interest to spectroscopists. When α-N_2, the form stable below 35.5 K, is bombarded with electrons, it emits light strongly as a series of bands, one of them at a wavelength very close to the auroral 5577 Å. The higher-temperature form β-N_2 does not show this behaviour. Vegard attributed the difference to rigid positioning of the molecules in α-N_2 but variable directions of the molecular axes in β-N_2 due to precession or rotation (39). Even though its emission of light when struck by electrons is very weak, the crystal structure of α-CO (40) was found to be very similar to that of α-N_2 – albeit with imperfect ordering of C and O atoms, giving rise to residual entropy (46). Likewise, the structures of β-CO and β-N_2 are very similar (40), both showing rotational motion.

5.2. *Results and controversies*

Of course, in the 1920s, even simple molecular structures were difficult to determine since computers were not available, and α-N_2 was the subject of controversy for several decades. Vegard reported (39) that DeSmedt and Keesom had obtained X-ray powder diffraction patterns from α-N_2 already in the mid-1920s but could not interpret them. Vegard described obtaining the eventual solution as "recht mühsam" (really arduous) (39). In a subsequent study Ruhemann (47) proposed a centrosymmetric structure for α-N_2 in space group Pa3 instead of Vegard's $P2_13$. The distinction hinged on two weak reflections, forbidden if the structure were centrosymmetric, which Vegard

claimed to have observed. A repeated powder diffraction analysis (48) failed to find significant intensity for these reflections and thus supported Ruhemann, but then a careful single-crystal structure determination by Jordan *et al.* (49) reconfirmed Vegard's $P2_13$, obtaining R-factors of 0.13 in this space group but 0.21 in Pa3. However, a study by Schuch and Mills (50) over a range of pressures did not reveal any evidence for a structure in $P2_13$. The identification of a noncentrosymmetric structure was then corroborated by the finding by Brookeman and Scott (51) of piezoelectric resonances in α-N_2. Finally, an electron diffraction study by Venables and English (52) attributed the observed deviations from Pa3 to twinning, and their choice of space group Pa3 now seems to be the preferred one.

Another wrangle arose over the structures of H_2S and H_2Se. Giulio Natta, later to become a famous polymer chemist, asserted (53a) that he had published (53b) the structures of these substances a few months earlier than Vegard. While they agreed on a cubic lattice with face-centred positioning of S and Se atoms, they disputed the space group of both and the density of H_2Se. Natta's postulate of ionic structures was wrong from the outset. However, Natta's density of 3.45 g cm^{-3} calculated from his X-ray data for H_2Se was close to the modern accepted value (54) of 3.553, while Vegard's reported value of 2.34 somehow was wrong.

The C-O and C-S bond lengths of 1.10 and 1.97 Å in Vegard's structure of COS (44) appear to be outliers and prompted a redetermination by neutron powder diffraction (55). Showing the difficulty of the problem, even with modern apparatus only 26 Debye-Scherrer peaks could be measured, some with incomplete resolution. The redetermined bond distances of 1.21(3) and 1.51(3) Å were now in accord with expectations.

6. Service to the physics community, the University of Oslo and wider society

One piece of evidence shows how very seriously Vegard was taken as a crystallographer by the physics community. A set of resolutions (56) adopted by a meeting of the International Union of Physics (now IUPAP) in 1931 included "Dr. Lars Vegard, of the University of Oslo, has been requested to prepare a special report on general questions concerning the bibliography, nomenclature, units, and symbols in crystallography." This work probably was eclipsed by the preparation under the auspices of the International Union of Crystallography of the International Tables for X-ray Crystallography, but from 1932 to 1940 he served as Vice President of the Union of Physics.

At a time when Norwegian auroral research was world-renowned but government funding was so scarce that an existing station was threatened with closure, Vegard's proposal to establish an auroral observatory in Tromsø attracted funding from the Rockefeller Foundation (57). Opened in 1930, it soon began to produce important results and achieve international prominence. As chairman of the relevant committee, he deserves credit for the successful development in the 1930s of the Blindern campus of the University of Oslo, which did much to facilitate the increase of the University in size and quality.
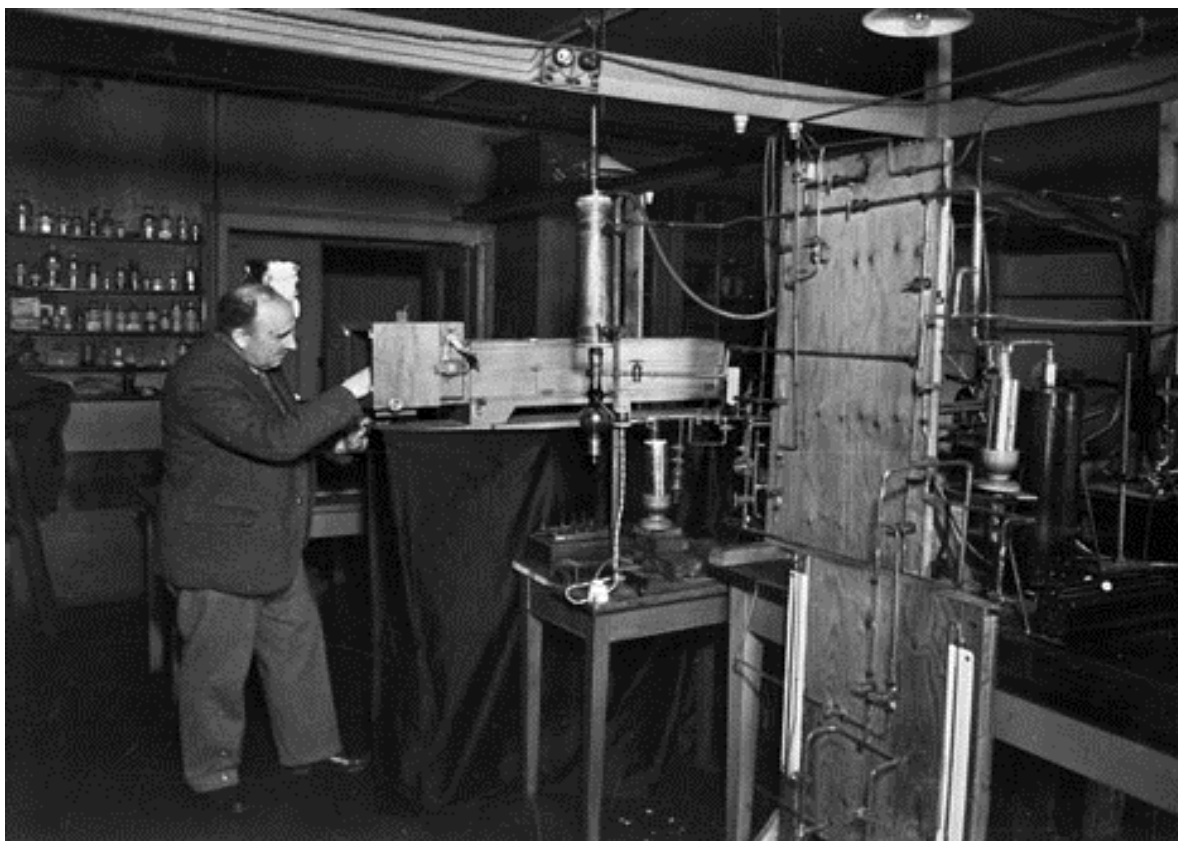

7. Personal qualities

Figure 5. Lars Vegard in his X-ray laboratory (6)

All his life, Lars Vegard loved to be outdoors and maintained a high level of physical fitness. Allied to dogged determination, these qualities were of great importance to his research into the aurora. He spent many frigid Norwegian winter nights outdoors with his spectrograph, in order to be ready to observe and record a display if and when it appeared. His detractors have described him as "pugnacious" and inclined to "use" his collaborators (2). There is some evidence in the physics literature that he could indeed be pugnacious. An early paper by Vegard and Schjelderup (58) on the crystal structure of alums showed that water molecules of hydration occupied definite positions in the lattice. Using spectroscopic techniques, Schaefer and Schubert (59) came to a similar conclusion and claimed priority. Not only did Vegard publish a critique (60) of this paper; when Schaefer and Schubert responded (61), he published a rebuttal (62). Differences between their proposed structures were slight; at issue were mainly questions of priority and whether crystallographic or spectroscopic methods gave more convincing results. Summaries of an exchange of letters with WLB in 1929 (63) demonstrate Vegard's concern that his papers should be correctly cited and Bragg's courteous concern to mollify Vegard: Vegard to WLB 21 May 1929 "In Bragg's treatment of salts of the substituted ammonias in the Annual Report of the Chemical Society, 1928, there is an erroneous reference to his papers; discusses this"; WLB to Vegard 29 May 1929 "Sorry reference to Vegard's work was omitted in their review for the Chemical Society. Is sending Vegard's letter to [J.D.] Bernal who was responsible for the section Vegard quoted"; WLB to Vegard 28 June 1929 "Has arranged with [J.D.] Bernal, who is going to do next year's Report for the Chemical Society, that the

mistake in the current report will be corrected. Apologises for the error. Impression given by Bernal's wording, which he agrees is erroneous, was unintentional. Bernal overlooked Vegard's 1927 paper."

It seems obvious that Vegard was never as generous to his co-workers as William Henry Bragg had been to him. The paper mentioned earlier (58) was somewhat unusual in that Schjelderup appeared as second author. (Harald Schjelderup later became the first professor of psychology in Norway.) Vegard was the sole author of most subsequent crystallographic papers from his laboratory, with a colleague occasionally appearing in second place. Co-workers were mainly mentioned in the acknowledgements at the end, although the kind words employed must have boosted their self-esteem and aided their future job prospects. Vegard's degree and doctoral student and long-time colleague Professor Godfrey Kvifte (1914-1997) rebutted criticisms of Vegard's treatment of his students by stating that he was an inspiring supervisor and sociable in casual situations (2).

As an administrator Vegard showed impressive vision, powers of persuasion and efficiency. It must be remembered that the bonanza of North Sea oil revenues only came to Norway much later. Between 1918 and 1935 Norway had nine governments, on average each lasting about a year and a half (64). It seems remarkable that in this environment Vegard obtained consistent support for a research programme that was world-class in both auroral and crystallographic studies. Already elected in 1914 to the Videnskabsselskabet (now the Norwegian Academy of Sciences and Letters), his contributions both to science and to wider society were recognised by his appointment as Commander of the Order of St. Olav in 1952 (65). He died in 1963 at the age of 83. In this 50th anniversary year it seems particularly appropriate that we should celebrate the life and work of this remarkable scientific polymath and linguist.

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