Part I: Jacob van Dijk **Enschede, 30 mei 2012**

⇨ ***chart 1***

Ladies and gentlemen,

It is a pleasure for both of us to hold this talk about professor dr E.W.Gorter (Evert) , whose name is probably not familiar to most of you. Frequently he is confused with either prof. E.Gorter (famous pediatrics/one of the first biochemists in NL – who happened to be his father) or Prof C.J.Gorter (Physics magnetic resonance – who is not a close relative).

We will do this presentation in two parts:

Jacob van Dijk: background + period at Philips Natuurkundig Laboratorium

Kees Plug: Professor Leiden crystal chemistry + conclusion

Our considerations to come to the choice of prof dr.E.W.Gorter are multiple:

- The title of this congress Fysica – Chemie 2012 suggests a strong interaction. This interface between chemistry and physics is exactly the field where Gorter made his most important contributions. This will stay as the red line during the presentation
- Prof. Dan Shechtman, Nobel Prize Chemistry 2011 give a plenary lecture tonight at the conference dinner. His fascination for crystal structures, symmetry / defects / (non)-periodicity reminds us very much to the thinking of Gorter
- Gorter was relatively young when he died which means he had no time to complete his scientific program
- This year we memorize Gorter's 100 year anniversary
- We were the first generation of student in inorganic chemistry under Gorter's professorate in Leiden. For us it is a kind of memory lane, which is fun to do. Please note we both are no professionals in history of science

⇨ **Chart 2**

⇨ **Chart 3**

The person Evert W. Gorter

Evert Gorter was born in 1912 as the son of a famous scientist. His father was professor Pediatrics in Leiden and first biochemist in Netherlands. He published several books and he was a scientific advisor for the consortium Philips-van Houten to commercialize vitamins incorporated in chocolate ***(note 1)***. This sounds like an ideal environment for the young adult Gorter but the relation with his father got strained. While his father wanted him to study physics it was Gorter himself, who decided to choose chemistry instead. Gorter did not accept advice from his father anymore and was determined to find his own scientific path.

Gorter studied at the Lyceum in Leiden and completed his studies with prof. A.E. van Arkel in inorganic chemistry in 1939. He was keen to receive a Ramsey Memorial fellowship at Manchester

University and awaiting a confirmation he was temporary employed as a teacher at Nederlandsch Lyceum in The Hague. (Coincidentally W.G.Burgers was also a Ramsey Memorial fellow in the period 1925-27). Gradually the threat of a new world war became stronger and stronger. Unlike WW I the Nazi's might not respect the Dutch neutrality. Gorter was happy to leave for the UK at 28 April 1940 at the brink of WW II! Remarkably Gorter with his wife and children were picked up by a Dutch military airplane

In England Gorter flourished and he adjusted to "Every inch a gentleman" being fluent in the English language and strongly anglophile. Nevertheless he was worried about his relatives, who stayed in the Netherlands

The eagerly wanted Ramsey fellowship started after arrival in UK with professor M.Polanyi at Manchester, who did research in reaction kinetics and the mechanism of chemical reactions. Gorter was studying oxidation reactions using O18.

Gorter's scientific career was strongly affected by the war. In 1941 he joins the Dutch army as member of the research group under the leadership of J.H.de Boer. This group was part of the English Ministry of Supply and housed in Imperial College of Science and Technology based in South-Kensington. Consequently Gorter moved to London. His direct superior was J.van Ormondt. Gorter studied argentic oxide reactants for carbon monoxide as a model system for chemical warfare. When the war came to an end the cooperation and information sharing about chemical warfare between the Netherlands and the USA/UK ceased to exist.

- ⇨ **Chart 4**

Ormondt and his reserve-first lieutenant Gorter were able to collect firsthand information themselves as Gorter was attached for some time as liaison manager to the Chemical Warfare staff of the Canadian 1st army. In this role both visited the German hot spots for chemical warfare. Also Gortre used this opportunity to look for strategically important laboratory equipment which the Germans had confiscated. ***(note 2)***

The period Philips Natuurkundig Laboratorium Eindhoven (1946-1964)

After the war the Dutch industry started energetically to recover the set-back caused the war. It was a period of intense contact between industry and universities. Examples are the careers of van Arkel / Holst / Casimir / Verwey / de Boer / … which were Philips related but also examples in connection with other industries are numerous. Gorter joined Philips Nat Lab in 1946 to participate in this burst of scientific energy.

At this time some of the key players in science of Philips which Gorter encountered are

- A.E. van Arkel (moved to already University Leiden): crystal chemistry / chemical bonding / thermodynamics/…
- E.J.W. Verwey: colloid chemistry / spinel structure/ magnetic properties /…
- J.H. de Boer: adsorption / material science /…

- ⇨ **Chart 5**

When Gorter started at Philips he became the part of a team working on ferrites. After some years he became team leader of the so-called “Magnetic Materials” group together with J.Smit (physicist). This team did build further on the fundamentals laid by Verwey, van Arkel and Snoek. The work on ferrites had already started before and continued during the war. The importance of ferrites as alternative to the existing metallic magnetic materials became more and more obvious.

Why were ferrites seen as so important?

- Offer unique applications due to combination of magnetic properties and electric isolator.
- After the war there was a shortage of certain metallic raw material as used in “ticonal”
- Ferrites offered the possibility to do all kinds of substitutions to manipulate the magnetic properties
- Ferrites were a novel area with huge patent opportunities

⇨ **Chart 6**

Crystal structure of spinel is a cubic closed packing (slight distortion) with half octaëder position and 1/8 of tetraëder positions occupied. The resulting anion coordination is a distorted tetraëder with explains part of the stability and possibilities for substitution. Gorter had a unique way of representing these crystal structures using his “blokje” but this will be discussed in the second half of the presentation

The magnetic properties are determined by the coupling of magnetic moments of cations in the different sub-lattices. In case all magnetic spins are oriented parallel this phenomenon is called ferro-magnetism. In case of an antiparallel orientation the resulting overall magnetic moment is zero and this is called anti-ferro-magnetism. It was Pierre Néel (Grenoble) who coined the term ferrimagnetism for a strong negative interaction, i.e. a tendency to antiparallel orientation for neighboring spins of ions on the tetraeder A and octaeder sites B . In case both coupled magnetic moments (M_A and M_B)are unequal there will be a non-vanishing magnetic moment ($M_A - M_B$). This (negative) interaction takes place via the anion and was recognized by H.A.Kramers and formalized in a theory by P.W.Anderson (1950) for this so-called super-exchange mechanism. Gorter and co-workers found strong experimental evidence to underpin the theory of Néel. Actually Gorter was personally in close contact with Néel during the years and visited him several times in Grenoble.

Some striking examples of Gorter’s experimental findings as presented in his thesis “Saturation magnetization and crystal chemistry of ferromagnetic oxides” Leiden 1954

⇨ **Chart 7**

Diluting the tetraeder sites with Zn (tetraeder preference) leads to a larger resulting magnetic moment. This observation is in line with Néel’s theory but rather unexpected that dilution with diamagnetic ion results in a higher overall magnetic moment (see: **note 3**)

⇨ **Chart 8**

The Néel theory also predicted various shapes of the resulting magnetic moment of the magnetic moment of the various sub-lattices as a function of the temperature. This phenomenon is shown in chart 6 where both temperature and magnetization are presented as dimensionless numbers for better scaling. Clearly there is a composition $Li_{0,5}Fe_{2,5-a}Cr_a0_4$ which shows that the overall magnetization passes zero at a certain temperature. In this context it goes too far to explain the details for the more interested person I refer to the literature (see: **note 4**)

Gorter has worked initially predominantly on cubic spinels, but he has also done significant work on hexagonal ferrites. In contrast to the cubic spinel, where the three axis are equivalent, the hexagonal ferrites had one specific symmetry axis which caused the spin to have a strong orientation resulting in permanent magnetic properties. This opened a new field for research and Gorter was keen to contribute. His proposes model to explain the magnetic moment due to the spin orientation is referred to as “Gorter’s model” (see: **note 5**).

- ⇨ **Chart 9**

He used the super exchange theory by Anderson to judge the strength of the interaction due to the angle between both cations and in between anion. His predictions were later confirmed with other techniques. This effect was the crux of Gorter’s approach where crystal structure and magnetic properties come together.

All his work at Philips found a place in his thesis (promotor A.E.van Arkel) which he defended 9 June 1954 which obtained the judicium “cum laude”. Unfortunately his father had just died shortly before this event. In a way he could not prove to his father that the route he had chosen to go was successful. His promotion was relatively late in his career and the war played here a key role.

In January 1964 he accepted a position as Professor Inorganic Chemistry in Leiden as successor to his teacher A.E.van Arkel. At that time the work on crystal chemistry at Philips had changed its character from explorative to more applied research to commercialize Ferroxcube (spinels) and Ferroxdure (hexagonal ferrites). Gorter must have felt the professorate was very timely for him. Apparently he was offered earlier a professorate at Imperial College London, which he turned down due to excessive educational costs for the 5 children. In a private correspondence (1954) with the Ramsey Memorial Fellowship Trust d.d. 25 August 1954 we read:

- ⇨ **Chart 10**

It is an so-called English understatement as the R&D work on ferrites has been of tremendous importance for Philips. Philips apparently licensed the ferrite patents to Bell AT&T (carrier wave technology) and received later in return access to the key transistor patents from Bell AT&T at a relatively low license fee. (see: **note 6**)

During his R&D work at Philips and therefor Gorter had developed himself much broader than a chemist. He enjoyed geology (mineralogy/earth magnetism /clays/…), culture in broader sense (Alhambra tiles with symmetry patterns / music / languages / ..) and international relations. The problematic side was his weak health (kidneys / starting deafness / weak heart). Despite these problems he happily moved to Leiden to start a new life.

Notes:

1. Pim Huijnen: "Het wondermiddel van professor Buytendijk" in Studium **4** , 162 (2010) note 25
2. Herman Roozenbeek en Jeoffrey van Woensel : 'De geest in de fles' Uitgeverij Boom (2010)
3. E.W.Gorter, Nature, **165**, 798-800 (1950)
4. E.W.Gorter H.A. Schulkes, Physica, **90** , 487 (1953)
5. E.W.Gorter Proc. IEEE **104B**, 255S (1957)
6. Marc J.de Vries: 80 Years of Research at the Philips Natuurkundig Laboratorium (1914-1994): The Role of the Nat. Lab. at Philips

For biography see:

An anthology of Philips Research Ed. H.B.G.Casimir & S.Gradstein:

a) Some main lines of 50 years Philips research in Physics by H.B.G.Casimir (pg 341-352)
b) Contributions of the Philips Research Laboratories to Solid-State Chemistry by H.J.Vink (pg 364-384)

DEEL II Kees Plug 30 mei 2012, Enschede

Plaat: inaugurele rede

As said before, in January 1964 Gorter accepted the position of Professor in Inorganic Chemistry at Leiden University. In his inaugural lecture, "Slithy Toves and the inorganic chemistry", he expresses how extremely honored he feels to be chosen as the successor of prof. A.E van Arkel, in his own words: his "teacher and friend". The title for this lecture derived the Anglophile Gorter from "Through the Looking Glass (And What Alice Found There)", by Lewis Caroll. Slithy toves in the nonsense poem Jabberwocky stand for "something very pretty, but rather hard to understand". And that is exactly the reaction Gorter expects by the audiency listening to his lecture on inorganic chemistry.

In the same lecture he also acknowledges the importance of the period of 17 years he could learn and work in the Philips NatLab, with its stimulating scientific culture. He also thanks the President of the University for his permission to use a part of his time for continuation of his contacts with the Laboratory in Eindhoven.

From his experience in the Philips Natlab, Gorter was very much aware of the importance to dispose of a well-equipped laboratory. He managed, as a condition for his coming to Leiden, to get money for a substantial modernization of the laboratory equipment, including a new X-ray diffractometer, a magnetometer operating at He-temperatures and a differential thermal analysis apparatus.

He was also aware of the need to give his field of research, the relation between the crystal structure and the physical properties of inorganic compounds, a sound base in solid state theory. Realizing that this theoretical approach was not his most important strength, he arranged that next to him a lecturer specialized in the theoretical inorganic chemistry could be appointed. This position was taken bij dr. Wim Maaskant.

In his inaugural lecture, Gorter shows, apart from his broad interest in non-chemical subjects, a thorough knowledge of the modern basis of inorganic chemistry . He acknowledges van Arkel, who in his view made a very important contribution to the transition in the inorganic chemistry from mere knowledge of facts to understanding the facts and their mutual relationship. From that point of view Gorter considers the task of an inorganic chemist the synthesis of new compounds and the investigation of its properties, when using his understanding of the chemical bonding and the crystal structures. “And it gives great satisfaction when these new compounds appear to be technical interesting materials “, we can hear the Philipsmade scientist say. But he continues: “A pleasure on a completely different level experiences a chemist when he finds something that he, using his understanding, was able to predict”.

Plaat: driehoek structuur – chemische samenstelling – fysische eigenschappen

This combination of understanding and the use of it in predictions is a very important theme in the work of Gorter. Knowledge of the crystal structure, understanding why it is as it is, relating this to physical (magnetic) properties and then predicting how for instance chemical substitutions will result in other structures and other physical properties. In this tradition examples are several PhD theses, for instance of Guus Schippers, Vas Brandwijk en Jan Arbouw.

A second important theme in the work of Gorter is the art of representing crystal structures. I use the word “art” by purpose, because the representation of a three dimensional array of atoms in such a way that the essence of it can be seen, is really an art that not many crystallographers have mastered. This gives rise to a communication problem. Gorter complains in his inaugural lecture: “Many crystallographers did very little effort to publish the crystal structures in such a way that chemists who want to use it can easily understand it.”

Plaat: foto van het Gorter blokje

Plaat: Gorter met het blokje

To overcome these problems, Gorter introduced so-called space-filling polyhedra (SFP), polyhedra that result from drawing midway planes between a crystallographic site and its neighboring sites of the same type.

The same type of polyhedron is used in solid state physics, where they in reciprocal space represent e the so-called Brillouin zone for electron density and are called Wigner-Seitz cells. The more general mathematical concept is called the Voronoi cell.

Plaat: lagen dichtste bolstappeling

Plaat: eenheidscel NaCl met aanduiding lagen A,B en C

The first advantage of the representation proposed by Gorter is the possibility to see readily the anion coordination by cations and the role the polarization of the anion plays in the crystal structure.

Plaat: blokje van NaCl en NiAs

For instance in the rock salt structure (ccp with all the octahedral interstices occupied) the anion is coordinated by a regular octahedron of cations, while in the structure of NiAs (hcp with all the octahedral positions occupied) the coordination polyhedron is a trigonal prism and the Ni-atoms form long chains through the structure. This may be an indication that cation – cation bonding plays a role in this compound. By filling all the tetrahedral positions in ccp (the vertices where three faces meet) with cations we obtain the structure of Li2 O; In hcp such a filling of all the tetrahedral sites is only possible with large distortions, since the cation-sites are too close to each other.

Plaat: blokje van MgCl2 en Cd(OH)2

The role of polarization can be seen in the structures for compounds in which only part of the cation positions is occupied, e.g. MX2 (or M3/6 X). In ccp the most symmetrical coordination is found in the structure of one of the forms of TiO2 (anatase), the most assymetrical coordination is found in MgCl,2, the Cl-anion having a higher polarizability then the oxygen anion.

Plaat: blokje van rutile en anataas

The second advantage of the use of the “Gorter blokjes” is the possibility to classify many existing structures into structural families, to describe and explain their differences and their similarities and to predict the change in crystal structure when changing stoichiometry or chemical composition.

Plaat (eventueel): blokje spinel

In his Leiden years the focus in Gorter’s work shifted from the relation between the crystal structure and magnetic properties of materials, to classification, representation and prediction of crystal structures in general. This is clearly reflected in the title of one of his most important and influential publications in this period, in the Journal of Solid State Chemistry (1970): “The Classification, Representation and Prediction of Crystal Structures in Ionic Compounds”.

In this paper no reference whatsoever is made to physical properties. Still, in the scope and titles of PhD-theses that were started during Gorter’s years in Leiden his continuated interest in the relation between structure and physical properties is reflected. “Magnetic investigations on some rare earth chalcogenides” (Arbouw). “Intercalation compounds of first row transition metal atoms” (Verhoeven). “Crystal chemistry and magnetic properties of ternary rare earth sulfides” (Plug).

Gorter most certainly had an eye for choosing interesting fields of research. Under his guidance, for instance, Gerard Ytsma carried out experiments in the system Sr – Cu – O in order to find missing structures by solid solution formation. Not much later this system turned out to be in the focal point of worldwide attention due to newly discovered superconducting properties. Of course Gorter was not aware of this but he was on a promising track.

Gorter also took a lively interest in so-called non-stoichiometrc compounds and the consequences of vacancies in the anion or cation lattices for the resulting crystal structures, including short-range ordering. His work on relating and predicting crystal structures was not restricted to relatively simple arrays of atoms, like ccp and hcp. He also studied more complicated structures in which 7- or 9-

coordinated polyhedra are observed. Gorter describes these less regular coordination polyhedra as the result of distortions of the structure in order to accommodate larger cations and/or changes in stoichiometry. It is interesting to note that Gorter's successor in Leiden, professor Bruce Hyde followed this track in a more systematic way, introducing shear structures, extended defects and regularly repeated twinning planes as structure-building entities which also result in 7- or 9-coordinated polyhedra. This similarity is illustrated by the drawings of two crystal structures, one of $CaFe_2O_4$ by Gorter, the other of $CaTi_2O_4$ by Hyde.

Plaatjes: $CaFe_2O_4$ en $CaTi_2O_4$ met 9-omringingen

Conclusion

On October 30 1972 Evert Gorter died, 59 years old and after a period of war oriented research, R&D teamleader at Philips NatLab and a professorship of only seven years. Due to serious health problems the effective period of his Leiden years was even much shorter. Because of this- and te reducing interest of Philips in crystal chemistry - there was not a real opportunity to build a full fledge "Gorter school" in Leiden (such as there most certainly was a van Arkel school). Still in our view Gorter 's professorate forms an important link in the Leiden tradition of Inorganic Chemistry.

His contributions in the two decades after WO II to the strong Dutch presence in the interface between solid state chemistry and solid state physics surely is worth remembering on Gorter's 100 year anniversary.

And for us, as two of the few students that graduated under Gorter's professorate, it was an honor to look back into the life and the work of our teacher and a pleasure to share this with you this afternoon.

Thank for your attention.