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Essay

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Perovskite: Name Puzzle and German-Russian Odyssey of Discovery

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Dedicated to Prof. *Michael Graetzel* on the occasion of his 75th birthday.

Today the term 'perovskite' is used to designate the crystalline structure of a wide variety of ABX_3 ionic compounds. However, historically this name was used for a specific material, having been coined for a mineral, calcium titanate ($CaTiO_3$). This mineral was discovered in the Ural Mountains, Russia. The first sample of the mineral was transferred from Saint Petersburg to Berlin in 1839 by the Russian mineralogist *Alexander Kämmerer*, who gave the sample for further investigation to the German mineralogist and crystallographer *Gustav Rose*. *Rose* determined its properties and chemical composition and named the mineral after the Russian politician and mineralogist *Lev Perovski*. The present essay describes the background of this discovery as well as the life stories of the personalities involved.

Keywords: perovskite, organic–inorganic hybrid composites, history of science, *Gustav Rose*, *Lev Perovski*, *August Alexander Kämmerer*, *Alexander von Humboldt*.

Introduction

The discovery of the metal halide perovskite (MHP) semiconductor as a photovoltaic absorber[1–3] and the subsequent meteoritic rise of the efficiency of solar cells based on this type of hybrid organic-inorganic materials[4–9] are among the most important scientific achievements of recent years.

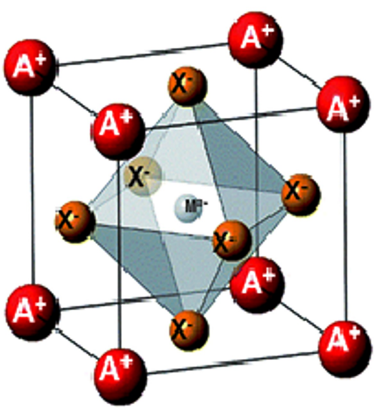

Figure 1. Unit cell of metal halide perovskite. Here, *A* is an organic or inorganic cation, *M* is a divalent metal cation, and *X* is a halide anion.

The MHP crystalline structure is represented by $[MX_6]_4^-$ an octahedral anion surrounded by organic cations (or inorganic) in a cubic or tetrahedral arrangement (*Figure 1*). Their general chemical formula is AMX_3.

The term 'perovskite' was coined for a calcium titanium oxide mineral composed of calcium titanate ($CaTiO_3$) (*Figure 2*). Today this term is used to designate a wide range of ABX_3 compounds with a similar type of ionic crystalline structure. Depending on the ion radii, the ideal cubic structure may deform to structures with lower symmetry. The perovskite structure can accommodate different dopant cations providing opportunities to turn the material properties.

The present essay describes the history of the $CaTiO_3$ perovskite discovery and the life stories of those people involved in it.

Figure 2. Mineral perovskite ($CaTiO_3$). *a*) Sample from mineralogical collection of the Museum für Naturkunde Berlin. Photo by *Hwa Ja Götz*. *b*) Sample from mineralogical collection of *P. A. Kochubey* (originally, probably from collection of *L. A. Perovski*). Now at the Fersman Museum of Mineralogy of the Russian Academy of Sciences, Moscow. Photo by *E. A. Katz*.

Discovery of the Mineral Perovskite

The $CaTiO_3$ mineral was discovered in the Ural Mountains of Russia. The first sample of the mineral was delivered from Saint Petersburg to Berlin in 1839 by the Chief Mines Inspector of the Russian Empire *August Alexander Kämmerer* (Александр Богданович Кеммерер) (1789–1858). *Kämmerer* gave the sample for further investigation to the German mineralogist and crystallographer *Gustav Rose* (1798–1873) (*Figure 3*) who determined its physical properties and chemical composition and even published an article.[10] On *Kämmerer*'s suggestion, *Rose* named the mineral after the Russian politician (Minister of Internal Affairs under Nicholas I of Russia) and mineralogist Count *Lev Alekseyevich Perovski* (1792–1856) (*Figure 4*). Today, this particular sample is part of the public exhibition of the Museum für Naturkunde Berlin (*Figure 1,a*).[1]

Figure 3. German mineralogist and crystallographer *Gustav Rose*. Photo from 'Wikipedia', public domain (https://en.wikipedia.org/wiki/Gustav_Rose#/media/File:Gustav_Rose.jpg).

Figure 4. Count *Lev Alekseyevich Perovski*. Photo from Wikipedia, public domain (https://ru.wikipedia.org/wiki/%D0%9F%D0%B5%D1%80%D0%BE%D0%B2%D1%81%D0%BA%D0%B8%D0%B9,_%D0%9B%D0%B5%D0%B2_%D0%90%D0%BB%D0%B5%D0%BA%D1%81%D0%B5%D0%B5%D0%B2%D0%B8%D1%87#/media/Файл:Lev_Perovsky.jpg).

[1] According to a private communication by Dr. *Ralf-Thomas Schmitt*, mineralogical collection of the Museum für Naturkunde (Berlin) contains two samples brought by *Kämmerer* in 1839 and investigated by *Rose*: sample 1999_0073 (9.5 cm × 5.5 cm × 5 cm, this particular one is shown in *Figure 2,a*) and sample 1999_0074 (7.5 cm × 5 cm × 2.5 cm). Both samples have original labels made by *Rose*'s hand. These two samples are interpreted as the type specimens for perovskite.

Gustav Rose

Gustav Rose was born in Berlin on March 18, 1798, in a family that counted at least four generations of distinguished scientists. His grandfather, *Valentin Rose* the Elder (1736–1771), pharmacist and chemist, was the founder of this scientific dynasty. He is known for inventing a low melting temperature alloy composed of bismuth, tin and lead, so-called *Rose* metal, today widely used as a solder. Since 1761, he owned and managed the pharmacy '*At the White Swan*' ('*Zum Weißen Schwan*') which was a real scientific laboratory. In 1771 a young journeyman and *Rose*'s assistant started to work in the pharmacy. It was *Martin Heinrich Klaproth* (1743–1817; *Figure 5*) who later became the first professor of chemistry at the University of Berlin. He is best remembered today for the invention of gravimetric analysis, the discovery of such chemical elements as uranium and zirconium, the co-discovery of titanium, strontium, cerium and chromium as well as confirming the previous discoveries of tellurium and beryllium. *Valentin Rose* the Elder died the same year, and *Klaproth* became the pharmacy manager and took over the care and education of *Valentin*'s two sons. One died while young; the other *Valentine Rose* the Younger (1762–1807) grew up to become a father of two sons himself: a chemistry professor in University of Berlin *Heinrich Rose* (1795–1864) and his younger brother *Gustav*, the main hero of our narrative. *Klaproth*'s own son *Julius* was a notable scientist as well[2].

The actual pharmacy '*Zum Weißen Schwan*' on Spandauer Straße in Berlin has not survived to this day. However, we can precisely identify its location since the pharmacy was situated just opposite to the oldest church in Berlin 'Heilige Geist Kirche' ('Holy Ghost Church', built in the XIV century) directly across the Spandauer Straße (*Figure 6*).

In 1780, *Klaproth* purchased the pharmacy '*Zum Bären*' ('*To the bear*'). In our context it is interesting that this pharmacy was previously owned by the famous chemist *Andreas Sigismund Marggraf* (1709–1782) who was *Valentin Rose* the Elder's teacher. This laboratory soon became the most productive research center in Europe in the field of artisanal chemistry.

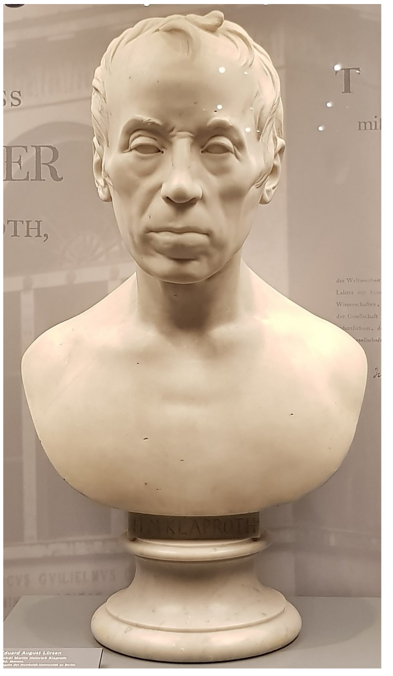

Figure 5. Bust of *Martin Heinrich Klaproth* at the Museum für Naturkunde Berlin. Photo by *E. A. Katz.*

Figure 6. On the left is Heilig-Geist-Kapelle, now belonging to Humboldt University (the part of Heilige Geist Kirche survived to this day). It faces Spandauer Straße. *Rose*'s pharmacy '*Zum Weißen Schwan*' was situated across the street at what is now a faceless multi-story building with shops on the ground floor. Photo by *E. A. Katz.*

This is where *Klaproth* performed his major work, including the discovery of uranium and zirconium.

Like '*Zum Weißen Schwan*', the remains of '*Zum Bären*' no longer exist, but we certainly know that it was at the end of Probst Straße (then called Probst Gasse), the street running directly along the Nicolas Church (Nikolaikirche) (*Figure 7,a* and *7,b*).

[2] *Heinrich Julius Klaproth* (1783–1835) was a linguist, historian, ethnographer, and orientalist who turned East Asian Studies into scientific disciplines with critical methods.

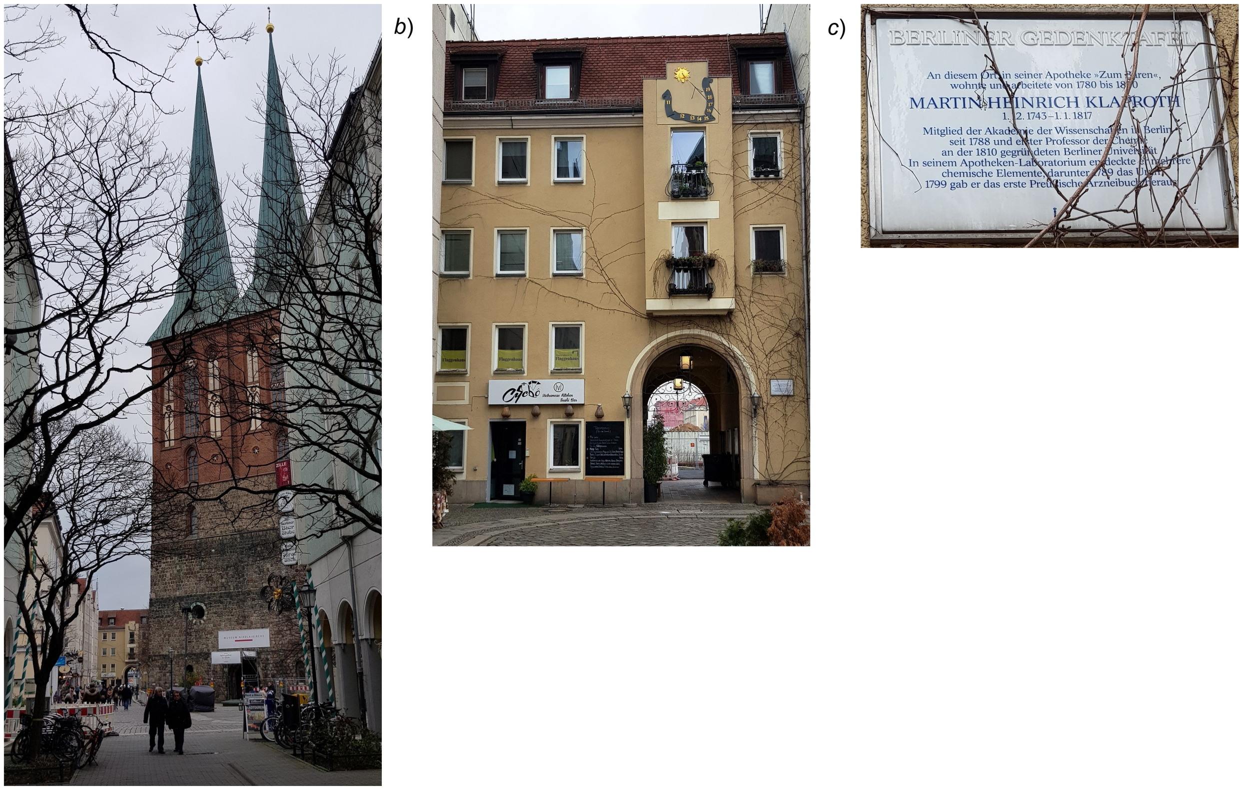

Figure 7. *a*). Probst Straße extending along the left side of Nikolaikirche. '*Zum Bären*' pharmacy was at the end of the street. *b*). The modern building at the place of '*Zum Bären*' pharmacy. A memorial plaque can be seen on the wall, to the right of an arch. c). Memorial plaque. Photo by *E. A. Katz*.

Today the site is marked with a memorial plaque (*Figure 7,c*) that states (in German; translated):

Berlin memorial plaque

At this site, in his pharmacy 'Zum Bären',

Martin Heinrich Klaproth

1.12.1743–1.1.1817

lived and worked from 1780 until 1800.

Member of the Academy of Sciences in Berlin from 1788 and first Professor of Chemistry in the Berlin University which was founded in 1810.

In this pharmacy laboratory, he discovered many chemical elements including uranium (1789). In 1799 he produced the first Prussian physician's manual.

Klaproth published extensively, in particular, over 200 papers which he collected in five volumes of 'Beiträge zur chemischen Kenntnis der Mineralkörper'.[11]

Brought up by *Klaproth*, *Valentin Rose* the Younger also listened to *Marggraf*'s lectures (at the Collegium medico-chirurgicum). In 1785 he became a provisor in '*Zum Weißen Schwan*' pharmacy, of which he gained ownership of in 1791. He is credited with the discoveries of several important organic compounds and the development of methods for their synthesis. He also developed a method for the detection of arsenic which would later be used in criminology.[12] Along with raising his own sons *Heinrich* and *Gustav*, correspondingly, professors of chemistry and mineralogy at the University of Berlin, *Valentin Rose* was a guardian of his younger cousin *Karl Friedrich Schinkel* (1781–1841)[3], probably the greatest architect of Berlin and one of the most prominent architects of all times in Germany.

Gustav Rose studied mineralogy at the *University of Berlin*, where he was a student of *Christian Samuel Weiss* (1780–1856). He also studied under the great physical chemist *Jöns Jakob Berzelius* (1779–1848) in Stockholm. While there *Gustav* met German chemist

[3] Mother of *Karl Friedrich Schinkel*, *Dorothea Schinkel* (born *Rose*) (1749–1800) was a sister of *Valentin Rose* the Elder.

Eilhard Mitscherlich (1794–1863)[4] (*Figure 8*) and they maintained a lifelong friendship and collaboration.[13] In particular, *Rose* assisted *Mitscherlich's* discovery of crystallographic isomorphism.

The discovery of isomorphism was significant for chemistry, mineralogy and crystallography. *Rose*'s and *Mitscherlich*'s supervisor *Berzelius* immediately used this concept to elucidate the atomic composition of solids (especially those comprised of R_2O_3 oxides). In determining the atomic weights of elements, isomorphism served as one of the important guiding attributes. The establishment of analogies between various elements found a significant help in the similarity of the crystalline forms of their compounds. Due to this, isomorphism became one of the main foundations of the Periodic table of chemical elements independently discovered a half of century later by *Dmitri Mendeleev* (1834–1907) and *Lothar Meyer* (1830–1895). With the discovery of isomorphism, the crystalline form has become a basis for characterization of solids. In particular, in minerology the discovery of isomorphism caused a significant revolution.

Gustav Rose stood at the origin of the isomorphism theory and then collected and analyzed minerals throughout his life.[5] That is why he was able to develop the 'crystal-chemical mineral system' using the isomorphism concept. The *Rose* system for the first time offered a way to organize minerals based on crystalline form and composition. He published two classical books on the topic: 'Elemente der Krystallographie, nebst einer tabellarischen Uebersicht der Mineralien nach den Krystallformen' ('Elements of crystallography, in addition to a tabular overview of the minerals according to the crystal forms')[15] in 1833 (*Figure 9*) and 'Das krystallo-chemische Mineralsystem' ('The crystal chemical mineral system') in 1852.[16]

The concept of the perovskite structure (as we understand it today) as comprised of various elements (ions) is a brilliant example of the application of the isomorphism idea. In our view, it is not a coincidence that the crystalline structure of the perovskite mineral was first described by Swiss-Norwegian mineralogist

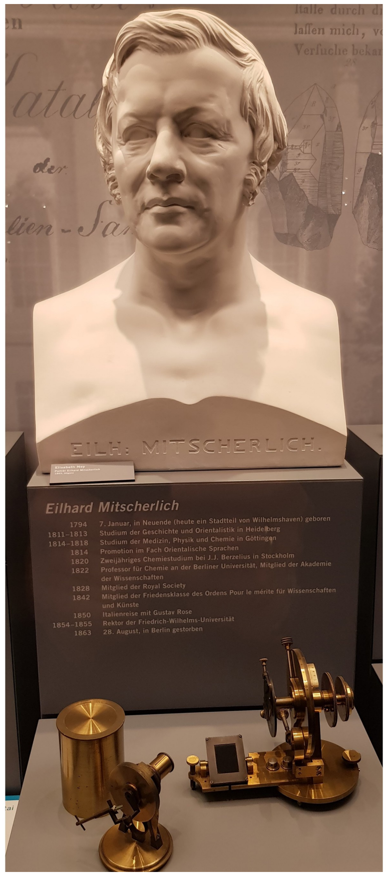

Figure 8. Bust of *Eilhard Mitscherlich* and his research instruments at the Museum für Naturkunde Berlin. Photo by *E. A. Katz*.

[4] *Mitscherlich*'s fantastic way to chemistry should be shortly mentioned. In 1811 he entered to the University of Heidelberg to study philology and, in particular, Farsi language. In 1813, he arrived in Paris and tried to get a permission to join the *Napoleon Bonaparte* embassy in Persia. The *Napoleon's* abandonment of the throne in 1814 destroyed this plan. *Mitscherlich* started to study chemistry in *Göttingen* to subsequently continue with medical education. His motivation was to get the traveling freedom allowed to physicians in the East at those times. However, chemistry attracted his attention so much that he abandoned the idea of traveling to Persia. During his stay in Göttingen, he wrote a treatise on Persian history. It was published in Persian and Latin in 1814 with the title 'Mirchondi historia Thaheridarum historicis nostris hucusque incognitorum Persiae principum'.[14]

[5] For the chemical analysis of minerals, *Gustav Rose* mostly collaborated with his older brother *Heinrich Rose*, chemistry professor in University of Berlin. *Heinrich Rose* rediscovered niobium and coined the name of this element.

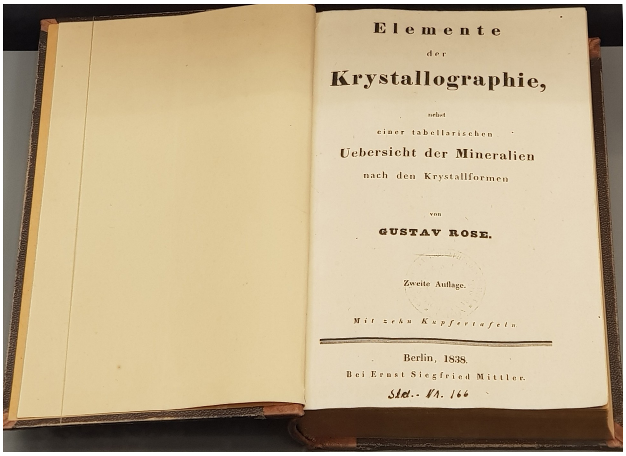

Figure 9. *Gustav Rose*'s book '*Elemente der Krystallographie, nebst einer tabellarischen Uebersicht der Mineralien nach den Krystallformen*' at the Museum für Naturkunde Berlin. Photo by *E. A. Katz.*

and geochemist *Victor Goldschmidt* (1888–1947)[6] (*Figure 10*) in his work on tolerance factors. Published in 1926,[17] this study made a fundamental contribution to the further development of the isomorphism theory. Originally formulated to describe the perovskite structure,[7] today *Goldschmidt*'s tolerance factor is used as an indicator for the stability of ionic crystal structure, in general. *Goldschmidt*'s rule postulates that complete isomorphism is possible only between atoms whose ionic radii differ no more than by 10–15%.

For our *perovskite* discovery narrative, it is of vital importance that that in 1829 *Gustav Rose*, along with *Christian Gottfried Ehrenberg* (1795–1876), accompanied the great naturalist *Alexander von Humboldt* (1769–1859)[8] (*Figure 11*) on his famous scientific expedition to the Ural mountains, Siberia and the region of the Caspian Sea of Russian Empire.[20] *Rose* oversaw the mineralogical studies. Meanwhile, *Ehrenberg* investigated micro-organisms in *Lake Baikal and the Caspian Sea. Humboldt* himself was keen to continue his studies of magnetism of mountains and mineral deposits.

They left Berlin on April 12 and arrived at St. Petersburg already on May 1. Initially, they followed the route: St. Petersburg - Moscow - Vladimir - Nizhny Novgorod - Kazan - Yekaterinburg – Perm (*Figure 12*).

Figure 10. Portrait of young *Victor Goldschmidt* (1909) by Norwegian artist *Asta Nørregaard* (1853–1933). Public domain.

[6] *Victor Moritz Goldschmidt* was born in Zürich in the family of the physical chemist and professor of the ETH *Heinrich Jacob Goldschmidt* and *Amelie Koehne*. In 1901, the family moved to Kristiania (today Oslo). *Viktor Goldschmidt* studied a wide range of scientific disciplines (from chemistry to botany and mathematics) at the University of Kristiania. In 1929 he took over the physical chemistry chair at the University of Göttingen. However, after the Nazis came to power he returned to Oslo. In 1942, *Goldschmidt* was arrested as a Jew by the German occupying powers and taken to the Berg concentration camp. Just at the moment of his deportation to Auschwitz, he was freed because some colleagues had managed to persuade the chief of police that his scientific expertise was essential to the state. *Goldschmidt* later fled to Sweden and eventually was flown to the UK by a British intelligence unit. He returned to Norway in 1946. After pioneering work on X-ray scattering by *Max von Laue* and *William L. Bragg* in the beginning of the XX century, *Goldschmidt* and his group of geochemists in Oslo were among the first who used this method to investigate the crystalline structure of minerals. In this way, he developed the basics for crystallochemistry. His publications in the series 'Geochemische Verteilungsgesetze der Elemente' ('Geochemical Laws of the Distribution of Elements') are considered as one of the foundations of geochemistry.

[7] In 1945, the crystal structure of perovskite mineral was revealed by X-ray diffraction data on barium titanate ($BaTiO_3$) by *Helen Dick Megaw* (1907–2002).[18] Another perovskite-type mineral, megawite ($CaSnO_3$), was named after her.[19]

[8] *Alexander von Humboldt* was a German polymath, naturalist, explorer, traveler, one of the founders of geography as an independent science. He was the younger brother of *Wilhelm von Humboldt* (1767–1835), the Prussian minister, philosopher and linguist, founder of University of Berlin Wilhelm von Humboldt.

They reached Kazan along the Volga River. The researchers spent several weeks in the Middle Ural devoting time to geological surveys and examining deposits of iron and gold ores, native platinum and malachite. The further route ran through Tobolsk, Barnaul, Semipalatinsk, Omsk and Miass. Then the expedition continued through the Southern Ural with a tour to Zlatoust, Orsk and Orenburg. Having visited the rock salt deposit in Iletsk, travelers arrived in Astrakhan and made a short trip along the Caspian Sea. They returned to St. Petersburg on November 13.

After returning from the trip to Russia, *Rose* intensively examined the collected minerals and rocks over the period of ten years. 117 different minerals were identified. Some of them (including cancrinite, rhodizite and chevkinite) were described for the first time. *Rose* summarized the results in the 1839 paper[10] and the book 'Trip to the Ural, the Altai and the Caspian Sea. By order of His Majesty the Emperor of Russia executed by A. von Humboldt, G. Ehrenberg and G. Rose in 1829: mineralogical-geognostic part and historical report of the trip' published in 1842 (*Figure 13*).[21]

Figure 11. Monument *Alexander von Humboldt* at Budapest Strasse, Berlin. Photo by *E. A. Katz*.

Figure 12. Map of the 1829 expedition to *Russia by Humboldt, Rose* and *Ehrenberg*. Adopted from Wikipedia, public domain (https://en.wikipedia.org/wiki/Alexander_von_Humboldt#/media/File:Humboldt_RUS.jpg).

There is no doubt that *Kämmerer*'s visit to *Rose* in 1839 with a request to explore a new mineral (later to be named perovskite) directly follows the expedition and *Rose*'s mineralogical activity and intensive contacts in Russia. Therefore, he included the newly identified perovskite in the paper devoted to the description of Ural minerals collected in the expedition.[10]

In 1850, *Rose* and *Mitscherlich* traveled with a geological purpose to Vesuvius, Etna and the Aeolian Islands. In 1852, *Rose* investigated the extinct volcanoes of Southern France.

Being a professor of University of Berlin, in 1856 *Rose* was appointed as a Director of the Royal Mineralogical Museum (*Figure 14*). He was President of the German Geological Society from 1863 till his death.

His sons, surgeon *Edmund Rose* (1836–1914) and the classicist *Valentin Rose* (1829–1916), constituted the fourth generation of the scientific dynasty.

Gustav Rose died on 15th of July 1873 and was buried at St. Marien and St. Nikolai I Cemetery (Friedhof Alter St. Marien - St. Nikolai) in Berlin. It is probably symbolic that *Rose*'s tombstone is made of a rose-color marble (*Figure 15*). Unfortunately, the inscription on his tombstone faded over time and can hardly be read:

'In memory of
Gustave Rose
Professor of Minerology at University of Berlin
18 March 1798–15 July 1873'.

However, his other monument is not in danger of time, and he will never require a restoration. This is the mineral roselite ($Ca_2(Co,Mg)[AsO_4]_2 \cdot H_2O$), named after the mineralogist (*Figure 16*).

Lev Alekseyevich Perovski

Lev Perovski was born on September 20, 1792. He was an illegitimate son of the Senator, Trustee of Moscow University, botanist, bibliophile and Freemason Count *Alexei Kirillovich Razumovsky* and the commoner *Maria*

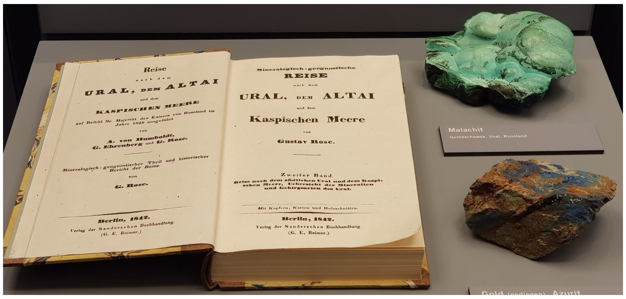

Figure 13. The 1842 book of *Gustav Rose* and some mineral samples from Ural mountains, at the public exhibition of the Museum für Naturkunde Berlin. Photo by *E. A. Katz*.

Mikhailovna Sobolevskaya. Officially, *Lev* and his three brothers and five sisters were considered as adopted children of their own father. Thus, a new noble family appeared, named after the village of Perovo, on the *Razumovsky's* estate. *Lev* and his younger brother *Vasily* were educated at Moscow University.

In 1812, *Lev Perovski* entered the military service as a non-commissioned officer. During the *Napoleon* invasion of Russia, known in Russia as the Patriotic War of 1812, *Lev Perovski* took part in the battle at Borodino and in all the major battles of this war as well as foreign campaigns of 1813–1814.

In 1818, the brothers joined the Decembrist Union of Prosperity. However, they did not participate in the later secret Decembrists' societies, and, apparently, did not support the military Decembrist Revolt[9]. On the other hand, the armed uprisings on December 14, 1825, were prepared by their former comrades, who regretted that *Lev Perovski* was not among them at the decisive moment.

After the uprising was suppressed, the new emperor *Nicholas I* did not punish the *Perovski* brothers for participating in the Union of Prosperity, but on the

Figure 14. *a*) In *Rose's* time, the Royal Mineralogical Museum was in the right wing of the present building of Humboldt University on Unter den Linden. *b*) In 1889, the museum collection moved into its permanent home and became a Mineralogical department of the Museum für Naturkunde. It contains an impressive collection of minerals (*ca.* 180,000 samples of *ca.* 3,000 mineral species, which is *ca.* 60% of all known minerals), including those owned by *Klaproth*, *Humboldt*, *Mitscherlich* and *Rose* with their original labels. Photos by *E. A. Katz*.

Figure 15. Gravestone of *Gustav Rose* at St. Marien and St. Nikolai I Cemetery (Friedhof Alter St. Marien - St. Nikolai), Berlin. Photo by *E. A. Katz*.

[9]The Decembrist revolt took place in Imperial Russia on December 14, 1825. Russian army officers led about 3,000 soldiers in a protest against *Tsar Nicholas I*'s assumption of the throne the day before, as his elder brother *Constantine* had removed himself from the line of succession. Because these events occurred in December, the rebels were called the Decembrists (Декабристы).

Figure 16. Mineral roselite ($Ca_2(Co,Mg)[AsO_4]_2 \cdot H_2O$), at the public exhibition of the Fersman Museum of Mineralogy of the Russian Academy of Sciences, Moscow. Photo by *E. A. Katz.*

contrary gave them high government posts[10]. Indeed, brilliant careers awaited both brothers during the reign of *Nicholas I*[11].

Already in 1829, *Lev Perovski* was appointed Vice-President of the Appanage Department of the Ministry of the Imperial Court, and in 1840 he became the deputy minister. The Appanage Department was established to manage the Imperial Family's estates and income. Starting from 1841, *Lev Perovski* combined his service in the Appanage Department with the post of Minister of Internal Affairs. He held this position longer than all his predecessors and successors in the *Nikolas I* reign.

Historians have very contradictory evaluations of the *Perovski*'s activity at these government positions.[22–25] A review of these opinions is beyond the scope of this essay. He was an extremely energetic person and enjoyed a reputation as an active opponent of the institution of serfdom.[12] Since 1842, his Ministry of Internal Affairs became the main headquarters for the preparation of the liberation of the peasants. This was confirmed by several legislative initiatives by *Perovski*, aimed at limiting and eventually the abolishing serfdom. In 1846, he prepared and submitted to the Emperor a comprehensive note 'On the cancelation of serfdom in Russia' ('Об уничтожении крепостного состояния в России'). Unfortunately, *Nikolai I* did not implement these reforms. Serfdom in Russia was abolished only after *Perovski*'s death, in the framework of the emancipation reform by *Alexander II* in 1861. However, there is no doubt that *Lev Perovski* was one of those who prepared this most important reform in the history of Russia of the XIX century.

The mining industry (including gemstone production) in the Russian Empire belonged to the Appanage Ministry. *Perovski* contributed much to the development of the mining and lapidary industries as well as mineralogy research in Russia. Many new deposits were mined because of his initiatives. He was one of the founders of the Mining Journal.

Being neither a chemist nor a mining engineer, *Lev Perovski* earned the glory of a zealous collector and a fine connoisseur of minerals. After the *Perovski's* death, his rich collection of minerals was bought by another ardent mineral collector, founder of the Russian Technical Society and honorary member of the Russian Imperial Mineralogical Society Prince *Petr Arkadievich Kochubey* (1825–1892).[26] This part of the collection is currently in the Fersman Museum of Mineralogy of the Russian Academy of Sciences, Moscow (*Figure 17*).

Along with perovskite, *Perovski*'s name was directly related to the discovery of two other minerals: phenakite (*Figure 18*) and alexandrite (*Figure 19*). All the unique vintage samples of these minerals from the

[10] The fates of the *Perovski* brothers in this sense were no exception to the general rule. *Nicholas I* made a decision worthy of a mature politician. He divided the participants of the Decembrist movement into those who dreamed of revolution and those who preferred liberal reforms. They did not participate in the uprisings and were not repressed. Moreover, many of them during the reign of *Nicholas I* occupied influential public posts. The historian *Vladimir Shkerin* called these liberals 'Decembrists without December'.[22] *Lev Perovski* became the most active liberal reformer during the reign of *Nicholas I* among the former members of secret Decembrist societies.

[11] *Vasily Perovski* (1795–1857) became governor-general of the Orenburg and Samara provinces.

[12] Term 'Serfdom in Russia' is a common translation of 'крепостное право в России'.'Serf' in this sense means an unfree peasant of the Russian Empire ('крепостной крестьянин') which meant an unfree person who, unlike a slave, could be sold only with the land he or she was 'attached' to. During his Russian expedition in 1829 *Alexander von Humboldt* was shocked by the living conditions of serfs and the very existence of serfdom in Russia. However, he could not freely report about it. This along with his disapproval of *Nicholas*'s restrictions on his freedom of movement during the expedition was among the reasons why *Humboldt* declined *Nicolas*'s invitation for second expedition to Russia.

Perovski–Kochubey collection are on the public exhibition at the Fersman Museum.

The mineral phenakite (Be_2SiO_4) was discovered in the Ural Mountains by the director of the Yekaterinburg lapidary factory *Yakov Kokovin* (1787-1840). Initially, the mineral was mistaken for a kind of quartz. It was *Perovski* who understood the difference between this newly discovered mineral and quartz and sent the samples for analysis to *Nils Gustaf Nordenskiöld*. *Nordenskiöld*,[13] who later described the mineral under a new name in 1833. I could not find a reference for that publication. In Russian literature (see for example [27]) it is believed that *Perovski* made the

Figure 17. Fersman Museum of Mineralogy of the Russian Academy of Sciences, Moscow. Photo by *E. A. Katz*.

Figure 18. Mineral phenakite (Be_2SiO_4), on public exhibition of the Fersman Museum of Mineralogy of the Russian Academy of Sciences, Moscow. Photo by *E. A. Katz*.

first description of the new mineral in the *Mining Journal* early in the same year.[28] However, reading this article, I did not find the author's name. On the contrary, I did find an indication that the paper is a translation of a nameless article published in the same year in *Annalen der Physik und Chemie*.[29] Subsequently, a detailed crystallographic description of phenakite was given by *Gustav Rose*.[30]

Alexandrite is a natural variety of the chrysoberyl mineral ($BeAl_2O_4$). It exhibits the effect of metamerism, displaying a color change dependent upon the nature of ambient lighting. Alexandrite from the Ural Mountains can be green by daylight and red by incandescent light. Other varieties of alexandrite may be yellowish or pink in daylight and a columbine or raspberry red by incandescent light. It was discovered in the Ural Mountains and first described by *Niels Gustaf Nordenskiöld* in 1842.[31] There is no disagreement in the literature on this subject. However, there are two versions of the history of the alexandrite discovery and naming. In both versions, *Perovski* was actively involved.[27]

According to a popular but controversial version, in April 17, 1834, *Nordenskiöld* received from *Perovski* a crystal of a strange color. At first, observing its dense green color and low refractive indices, *Nordenskiöld* decided that it was not a completely intrinsic emerald. However, he measured unexpectedly high values the sample hardness (8.5 instead of 7.5 characteristic for the emerald). Unable to finish the analysis on the spot, *Nordenskiöld* put the sample in his pocket, deciding to study it later. Later that evening, he took out the crystal to observe it under the candles light. However, instead of a green crystal, he had a bright red one in his hands.

According to another, probably more realistic version,[27] alexandrite was found for the first time in

[13] *Nils Gustaf Nordenskiöld* (1792–1866) was Finnish mineralogist, chemist and mining engineer serving in the Russian Empire, Corresponding Member of the Russian Academy of Sciences, founder and president of the Finnish Scientific Society. He is known as the author of the atomistic-chemical classification of minerals. *Nordenskiöld* described many new mineral species and their physical and chemical properties. He was the first to conduct a chemical analysis of a meteorite in 1821 and established the unity of terrestrial and extraterrestrial elements. His name will appear in our narrative more than once.

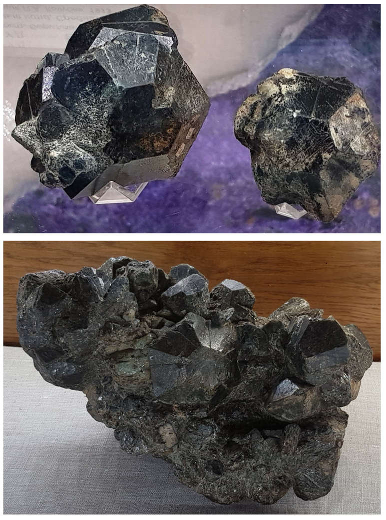

Figure 19. Mineral alexandrite, variety of chrysoberyl ($BeAl_2O_4$) doped by chromium, on public exhibition at the Fersman Museum of Mineralogy of the Russian Academy of Sciences, Moscow. *a*) Crystals of alexandrite. *b*) Unique druse consisting of 22 alexandrite crystals. Size of the largest crystal is 7.5 cm. Photos by *E. A. Katz.*

an emerald mine on the Tokovaya River near Yekaterinburg in 1833 by *Yakov Kokovin*. He described it as an emerald and sent it to *Perovski*. Confused by its higher degree of hardness, *Perovski* also noted a color change. Initially, *Perovski* planned to name the new mineral 'diaphanite' (from Greek *διαφανής* – 'brilliant, bright'). However, taking advantage of the moment, he coined the name 'alexandrite' and presented it to Grand Duke *Alexander* at his 16th birthday on April 17, 1834.

August Alexander Kämmerer

August Alexander Kämmerer (Александр Богданович Кеммерер) was born in 1789 in the Thuringian town of Artern (then belonging to Saxony). *Kämmerer* was brought to St. Petersburg by parents at the age of eight. After receiving his initial schooling, he enrolled as a pupil in a private pharmacy. In 1809 he passed the exam for a pharmacist, and already in 1812, he opened his own pharmacy. His busy practical activity did not prevent *Kämmerer* from devoting himself to scientific studies. He was the Chairman of the Russian Pharmaceutical Society, in the founding of which in 1818 he took an active part, as well as a member of the Russian Imperial Mineralogical Society and the Moscow Society of Naturalists.

In 1824, he became the chief-chemist at the laboratory of the Department of Mining and Salt Affairs, and then, in 1826, he headed the newly founded Main Mining Pharmacy. This new position allowed *Kämmerer* to devote most of his time to his favorite activity – mineralogy. He published many articles in the *Mining Journal* (Горный Журнал) and the *Proceedings of the Russian Mineralogical Society* (Записки Российского минералогического общества). For the work 'Ueberblick der Theorien der Geologie Werner's und Hutton's' ('Overview of the theories of Werner's and Hutton's geology') Heidelberg University awarded him a PhD degree in 1829. Later the dissertation was published as a paper in the *Mining Journal*.[32]

In 1829, at the behest of Emperor *Nicholas I* of Russia (1796–1855), *Kämmerer* started to teach some basics of natural sciences to Grand Duke *Alexander Nikolayevich*, later Emperor *Alexander II* of Russia (1818–1881).

Kämmerer gathered an excellent collection of minerals, mostly from Russia. One of the latter examples in that collection was a type of pennin found in the Ural Mountain>s. It was first described by *Nils Gustaf Nordenskiöld* in 1842[32] and named after *Kämmerer* (*Figure 20*).

We certainly know from *Gustav Rose*'s publication[10] that the new mineral (which eventually came to be known as perovskite) brought to him by *Kämmerer* in the summer 1839 was found in the South Ural Mountains, at the mine 'Akhmatovskaya Kop' (Ахматовская Копь) near Zlatoust (Златоуст) (*Figure 21,a*). This mine was discovered in 1811 by *Efim Akhmatov*, the Director of the *Kusinskiy Iron Works* near Zlatoust.[34] During the XIX century it was extensively used as a source of valuable mineral specimens. Its detailed description was published in 1878 by the Russian explorer and geologist *Ivan V. Mushketov* (1850–1902).[35] In 1981, it was declared as a state-protected geological monument in the framework of the National Park 'Taganay' ('Таганай') (*Figure 21,b*).

From the same source,[10] we know that *Gustav Rose* named the new mineral after *Lev Perovski* upon *Kämmerer*'s suggestion. What preceded *Kämmerer*'s visit to Berlin? Who found the samples of the new mineral in Russia? From whom did *Kämmerer* receive these samples? These questions remain open. Based on the above stories of the discoveries of phenakite and alexandrite, I venture to suggest that *Lev Perovski* was somehow involved.

Figure 20. Mineral kämmererite ($Mg_5Al(AlSi_3O_{10})(OH)_8$), at the public exhibition of the Fersman Museum of Mineralogy of the Russian Academy of Sciences, Moscow. Photo by *E. A. Katz*.

In lieu of conclusions

In 1845 *Alexander von Humboldt* wrote: 'Every law of nature that reveals itself to the observer suggests a higher law, yet unknown'.[36] Without the discovery of the mineral perovskite and the subsequent studies in the XIX century, many of the outstanding achievements of modern science would not have been possible. In 1987, the *Nobel Prize in Physics* was awarded to *Georg Bednorz* (1950) and *Alex Müller* (1927; both from the *IBM Research Laboratory*, Zurich, Switzerland) for the discovery of High Temperature Superconductivity (HTSP). Their *Nobel* Lecture was titled: 'Perovskite-Type Oxides: The New Approach for High-Tc Superconductivity'.[37] Another *Nobel* Prize in physics (2007) was awarded for the discovery of Giant Magnetoresistance (GMR), an abnormally high change in resistance of a conductor when it is placed in an external magnetic field. This quantum mechanical effect is observed in an alternating sequence of ferromagnetic and non-magnetic conductive nanolayers.[38,39] The discovery of the GMR effect gave rise to an increased interest in finding related effects among bulk materials. Resistance change in an applied magnetic field several magnitudes higher than for GMR was observed in certain manganese perovskites.[40–44] The observed phenomenon became known as colossal magnetoresistance (CMR). We appreciate what is happening right before our eyes, which is the development of highly efficient photovoltaics based on metal halide perovskites[1–8] as the third 'perovskite revolution' of modern time. A *Nobel* Prize is to be expected.

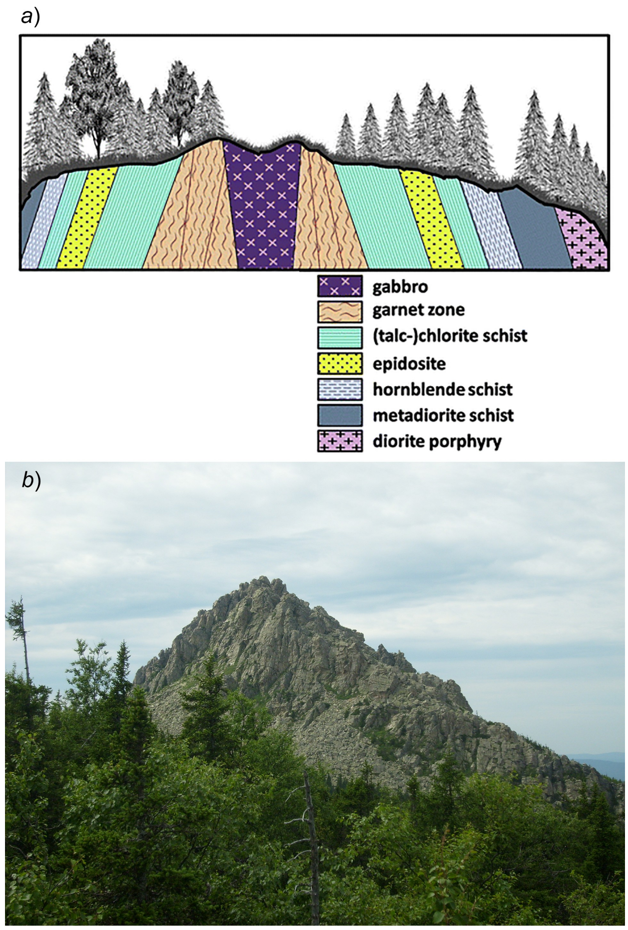

Figure 21. *a*) Schematics of the mine 'Akhmatovskaya Kop', as it was seen by Ivan Mushketov in 1878.)[35] Reproduced from Ref. [34] with permission of *Springer-Verlag*. *b*) At the National Park 'Taganay'. Photo from *Wikipedia*, public domain (https://ru.wikipedia.org/wiki/%D0%A2%D0%B0%D0%B3%D0%B0%D0%BD%D0%B0%D0%B9_(%D0%BD%D0%B0%D1%86%D0%B8%D0%BE%D0%BD%D0%B0%D0%BB%D1%8 C%D0%BD%D1%8B%D0%B9_%D0%BF%D0%B0%D1%80%D0%BA)#/media/Файл:Откликной_гребень.jpg).

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