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we added successively in concentrations of 1 mol. percentage, the following chemically pure preparations:

		Observed and reduced Meltingpoints:
1. *Jadeite*: $NaAlSi_2O_6$, synthetical.		14415 M.V. = 1382°
2. *Leucite*: $KAlSi_2O_6$, synthetical, anhydrous.		14506 M.V. = 1414°
3. *Lithiumoxide*: Li_2O.		14304 M.V. = 1397°
4. *Alumina*: Al_2O_3.		14585 M.V. = 1420°
5. *Silica*: SiO_2 (quartz).		14530 M.V. = 1416°
And in concentrations of 2 mol. perc.:		
6. *Pseudowollastonite*: $CaSiO_3$, synthetical.		14357 M.V. = 1402°
7. *Sillimannite*: Al_2SiO_5, synthetical.		14593 M.V. = 1421°

Keeping in mind, that the pure substance melts at 1417° C. (G. Th.), we can deduce from these experiments, that:

a. An excess of Li_2O *lowers* the meltingpoint of the compound $LiAlSi_2O_6$, while the influence of an excess of SiO_2 is somewhat uncertain, but seems to produce a *slight increase*.

b. That a *lowering* of the meltingpoint is also produced by an excess of synthetical *jadeite*, *leucite* and *pseudowollastonite*, which can be considered as the principal admixtures of the natural kunzites and spodumenes.

c. That on the contrary, an *increase* of the meltingpoint is produced by an excess of *alumina* and of *alumosilicates*, like e. g. pure *sillimannite*.

In how far these facts, which of course will be studied more in detail, when the ternary system: $Li_2O-Al_2O_3-SiO_2$ is investigated completely, can be used for the explanation of the phenomena, observed in the case of the natural spodumenes, will be shown in the next paper.

Groningen, May 1914.　　*Laboratory of Inorganic Chemistry of the University.*

Chemistry. — *"Studies in the Field of Silicate-Chemistry. III. On the Lithiumaluminiumsilicates, whose composition corresponds to that of the Minerals Eucryptite and Spodumene".* By _Prof. Dr. F. M. JAEGER and Dr. ANT. ŠIMEK. (Continued). (Communicated by Prof. P. van ROMBURGH.)

(Communicated in the meeting of May 30, 1914).

§ **12.** For the purpose of comparison of the properties of the described artificial product with the mineral itself, we have investigated a number of natural *spodumene*-species in an analogous way.

We obtained a number of very pure *kunzites*, and some good *spodumenes*:

1. An almost colourless, somewhat lilac tinged, strongly dichroïtic *kunzite* from *Rincon* in *California.*

2. A completely transparent, glassy, pale rose tinged *kunzite* from *Sahatany*-valley on *Madagascar*.

3. A beautiful, transparent pale greenish yellow *kunzite* from *Minas Geraës* in *Brasil*.

4. A transparent, emerald-green *hiddenite* from *Alexander County* in *North Carolina*, U.S.A., and a pale yellow hiddenite of the same place.

5. A cryptocrystalline, opaque piece of *spodumene* from *Somerö*, in *Finland*.

6. An aggregation of opaque, long prisms of *spodumene* from *Maine*, U. S. A.

All meltingpoints of the finely ground material were determined in exactly the same way and with the same care, as formerly described. The specific gravities were determined by means of a pycnometer, with ortho-chlorotoluene as an immersion-liquid; the specific gravity of this was: $d_4^0 = 1,0841$ at $25°,1$ C.

Most of the optical data were obtained by microscopical investigation; the values of the refractive indices are determined at 16° or 17° C.

I. *Kunzite of Rincon, California.*

Big, very feeble lilac colours, very lustrous and perfectly transparent crystals, evidently with a cleavage parallel to the vertical prism. An analysis of *Davis*, made with the same material, gave the following results :

		Calculated:	*Impurities* :	
SiO_2	: 64,05 %	64,6 %	CaO : 0,8 %	MnO : 0,11 %
A_2O_3	: 27,30 %	27,4 %	Na_2O: 0,3 %	NiO : 0,06 %
Li_2O	: 6,88 %	8,0 %	ZnO : 0,44%	K_2O : 0,06 %

Total: 0.78 %.

The crystals show a strong fluorescence under the influence of RÖNTGEN-rays.

The meltingpoint determinations gave, with thermoelement IV, the following results: as a mean value of a greater number of observations, we found : 14683 M. V. ± 4 M. V.; as the correction of the thermoelement at this temperature was — 8 M.V., the melting-point is thus: 1428° C. (G. Th.). It is very sharply localised on the heating-curves.

The specific gravity at 25,1° C. was: $d_4^o = 3.204 \pm 0,003$ for the natural, not yet melted compound; after solidification of the molten mass, one obtains, after slowly cooling, a colourless, finely crystallized mass, whose density differs considerably from the original mineral; it is: $d_4^o = 2,385$ at 25°,1 C.

The refractive indices of the molten and solidified substance are considerably different from those of the original mineral. While for the unmelted substance we found respectively: $n_1 = 1,653 \pm 0,003$, $n_2 = 1,669 \pm 0,003$; and $n_3 = 1,672 \pm 0.003$ [1]), for the solidified mass we found an extremely feeble biréfringence of about 0,001, and a mean refractive index of: $n_D = 1,518$. The crystalpieces showed an irregular extinction, evidently by very complicated intergrowth of several individuals.

On rapidly cooling, an isotropous *glass* was obtained, with a refractive index of $n_D = 1,517 \pm 0,001$, being about the same as for the crystallized mass. The specific gravity was at 25°,2 C.: $d_4^o = 2,388 \pm 0,003$. When heated during a longer time at 1300° C., it becomes crystalline; even at lower temperatures the glass gets soon opaque and like porcelain by devitrification; but glass and crystalline product obtained from it, evidently do not differ in their properties to any appreciable amount.

II. *Kunzite of the Sahatany-valley on Madagascar.* Big, clear and completely transparent crystals; they are dichroitic and tinged with a pale rose hue. Locally the environing rock-material is again discernible, as a rusty coloured, finely divided substance. The crystals were carefully cleaned from it; then they were ground and sieved, after which the investigation proceeded in the usual manner.

As a mean value for a greater number of determinations, we found the meltingpoint at: 14683 ± 5 M.V.; as the correction of the thermoelement was — 8 M.V. at this temperature, we can adopt the value 14675 M.V. of the E.M.F. of the thermoelement at the meltingpoint, corresponding with: 1428° C. (G. Th.); in this case the meltingpoint is also very sharp.

Evidently this kunzite differs only slightly from the preceding mineral of *Rincon.* With respect to its chemical composition, we have some data, given by Lacroix [2]), who investigated colourless,

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[1]) In a liquid of $n_D = 1,670$, composed of methylene-iodide and monobromo-naphtaline, the crystalpowder showed a very beautiful reddish-violet colour, just as some of Christiansen's "monochromes". The same phenomenon was observed for the glass and the β-modification of artificial spodumene.

[2]) A. Lacroix, Minéralogie de la France et ses Colonies, IV, 775, (1910).

greenish-yellow and rose kunzites (triphane) from *Maharitra* on *Madagascar*; the lilac and rose kunzites of *Ampasihiatra* are imbedded in a kind of kaoline-earth, generated from the spodumene by decaying-processes. The green kunzites possess the greatest values of their refractive indices, however only little differing from the other ones, while the rose tinged crystals have a smaller, the colourless ones yet smaller values for those constants.

We found by means of the immersion-method $n_1 = 1,658$ and $n_2 = 1,673$, which values do not differ appreciably from the mean values: $n_1 = 1,6588$, $n_2 = 1,6645$ and $n_3 = 1,6750$.[1]) For the analysis of the red and greenish crystals, the following data are given in literature; they are reproduced here for comparison with the composition of the Californian kunzite:

rose cristals:		green cristals:	
SiO_2 : 63,85% CaO : 0,52% MnO : trace		SiO_2 : 62,21% CaO : 0,50% MnO : trace	
Al_2O_3: 29,87% Na_2O 0,98% Fe_2O_3:0,15%		Al_2O_3: 29,79% Na_2O: 1,03% Fe_2O_3:2,48%	
Li_2O : 3,76% MgO :0,13% K_2O :0,13%		Li_2O : 4,02% MgO : trace K_2O :0,21%	
Residue: 0,37%.		Residue: 0,25%.	

From these data results, that the quantity of SiO_2 in the rose crystals is about the same as for the pale rose kunzite of *Rincon*; but the content of Al_2O_3 is much greater in the mineral of *Madagascar*, and thus the Li_2O appreciably less than in the American kunzite. The sum of those three constituents does not differ very much in all these cases: 97,5 % for the kunzite of *Madagascar*, 98,2 % for that from *Rincon*. The specific gravity of the rose species is about 3,177; — a value, only slightly different from the value, determined by us: $d_4° = 3,301 \pm 0,005$, at 25°,1 C.

The refractive indices of the melted, feebly birefringent product, were found to be $n_1 = 1,518$ and $n_2 = 1,520$; the birefringence is not greater than 0,002.

At 25°,1 C. the specific gravity of the melted and solidified substance was determined: $d_4° = 2,373$, when the preparation was heated during several hours at a constant temperature, just below the meltingpoint; under the microscope the obtained product then showed the typical aspect of the aggregates of scales, which are always found with the β-spodumene; they have a weak birefringence, and an irregular, often undulatory extinction. When α-spodumene was *not* melted before, but only kept at a constant temperature below the meltingpoint, the substance appeared to be wholly transformed into the same β-modification, with a specific gravity of: $d_4° = 2,376$ at

[1]) Duparc, Wunder et Sabot, Mém. de la Soc. physique de' Genève, **36**, 402, (1910).

25°,1 C. In both cases the mean refractive index for sodiumlight was: $n_D = 1,518 \pm 0,001$. From the molten mass therefore no other phase is deposited than the mentioned β-modification.

The fig. 5, 6, and 7 may give an impression of the manner, in which the transformation of the α-, into the β-modification gradually occurs. In fig. 5 the original kunzite of *Madagascar* is photographed between crossed nicols, when heated only during 2 hours at 975° C., and showing no trace yet of the β-form; in fig. 7 the same heating, but prolonged to 15 hours, has led to complete transformation of the .crystals into the β-form. The fig. 6 represents the crystals, after 8 hours heating at 975° C.; they show a partial transformation, and the gradually occurring differentiation of the originally homogeneous crystals into an aggregation of the felty needles of the β-modification.

III. *Greenish-yellow Kunzite of Minas Geraës, Brasil.*

This kunzite appears also in the form of large, very transparent crystals, having a pale greenish or yellowish hue. This colour is caused by a content of FeO, which in melting the mineral, is converted into: Fe_2O_3; thus the solidified mass being always tinged with a reddish-brown colour. The analysis of this mineral [1]) gave the following data :

SiO_2 : 63,3—64,3%		CaO : 0,2—0,7 %
Al_2O_3 : 27,7—27,9%		Na_2O : 0,6—1,0 %
Li_2O_3 : 6,7— 7,4%		FeO : 0,7—1,2 %

This kunzite therefore is also relatively close in composition to that of *Rincon*, approaching in its content of Li_2O closer to the theoretical value; the sum of the principal constituents is 97,7 %.

The meltingpoint of this mineral was determined five times; the results were, with thermoelement IV :

$$14643 \text{ M.V.}$$
$$14646 \text{ M.V.}$$
$$14650 \text{ M.V.}$$
$$14639 \text{ M.V.}$$
$$\underline{14646 \text{ M.V.}}$$

Mean value: 14645 M.V.;

after correction : 14637 M.V. (G. Th.)

The meltingpoint, reduced on the nitrogengasthermometer, lies thus at 1425° C., i. e. about 3° C. lower than for the kunzite of *Rincon*.

The specific gravity of the substance before melting, was determined at 25°,1 C. to be: $d_{4^0} = 3,262$; the data, given in literature for the specific gravity of natural crystals, vary between 3,16 and

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[1]) C. Hintze, Handbuch der Mineralogie.

3,174. The refractive indices of the original substance were: $n_1 = 1,661$ and $n_2 = 1,669$, with apparently a somewhat weaker birefringence as for the already described kunzites.

Fig. 5.
Kunzite of *Madagascar*, heated for two hours at 960° C. and not yet perceptibly transformed. (✕ Nicols).

Fig. 6.
Beginning of the transformation of *x*-spodumene (*Madagascar*), after being heated during eight hours at 975° C. (✕ Nicols).

Fig. 7.
Kunzite of *Madagascar*, completely transformed into the β-form, after being heated at 975° C. (✕ Nicols).

After being melted however, the reddishbrown, crystalline product had a specific gravity at 25°,1 C.: $d_{4^0} = 2,463$, while the refractive indices of the feebly birefringent grains were found to be about 1,522 and 1,527. There is no doubt whatever about the fact, that the solidified product is again a modification absolutely different from the original kunzite; moreover it is evidently identical with the already mentioned β-spodumene.

IV. *Hiddenite from Alexander County, North Carolina, U.S.A.*

Long, needle-shaped, pale green crystals, and emerald-green crystal-fragments, which are transparent and dichroitic. The specific gravity of this mineral at 25°,1 C. was found to be: $d_{4^0} = 3,295 \pm 0,002$; the refractive indices were: $n_1 = 1,664$ and $n_2 = 1,674$. The data for the specific density, given in literature, vary between 3,152 and 3,189. Of a hiddenite from *Alexander City*, with specific weight of: $d_{4^0} = 3,177$, the analysis gave the following results:

SiO_2	: 63,95 %	FeO	: 1,1 %
Al_2O_3	: 26,58 %	Na_2O	: 1,54 %
Li_2O	: 6,82 %	CaO	: no trace.

The sum of the principal constituents is here 97,35 %; the hue of the crystals is caused by the admixture of FeO, which is oxydized in melting to Fe_2O_3, giving a brownish-black or chocolate-brown colour to the solidified mass. Another hiddenite of the same locality, but of a paler colour, had: 64,35% SiO_2, 28,10% Al_2O_3, and 7,05% Li_2O, — consequently together · 99,5 %; moreover: 0,25 % FeO and only about 0,3 % Na_2O. The differences of the meltingpoints of these two kinds of hiddenite, were about 1° C. or less. In a series of observations, made with thermoelement IV, the melting-point was found at 14565 M. V. $\pm$ 10 M. V.; after correction, this corresponds to 1418° $\pm$ 1° C. (G.Th.). On cooling down the molten mass, first an undercooling is observed to about 1255° C., if the temperature-fall was about 4° pro minute; then the temperature rose to 1262° C. during the solidification of the mass, being 150° C. lower than the real equilibrium-temperature.

Another time we found an undercooling to 1208° C., then solidification at 1214° C., — this being 204° C. lower than the true meltingpoint! Although this point of solidification is lower than that for the pure kunzites, it can have no essential signification whatever, being wholly dependent ·on the speed of cooling and other accidental circumstances.

V. Spodumene of Somerö, Finland.

A white, opaque cryptocrystalline and very hard mass. It was finely ground, and investigated in a manner, quite analogous to that formerly described. The specific gravity at 25°,1 C. was: $d_{4^0} = 2,997 \pm 0.050$; the refractive indices were about: $n_1 = 1,658$ and $n_2 = 1,669$. With the thermoelement IV the meltingpoint was found at 14649 M.V. $\pm$ 5 M.V.; being, after correction, 1425° C. on the gasthermometer. Because of the inhomogeneity of the material, the meltingpoint is here not so sharply localized on the heatingcurves, as in the cases of the kunzites; on cooling the molten mass, solidification occurs in the neighbourhood of 1298° C.

The substance solidified and heated for some hours below its meltingpoint, had a specific gravity at 25°,1 C. of: $d_{4^0} = 2,398$; the refractive indices were about: 1,510 and 1,518 for sodiumlight, — just a little smaller than commonly with the β-spodumene. The substance always shows very complicated aggregations of feebly extinguishing scales with undulatory extinction.

If the original substance is not melted, but only heated during a longer time below its meltingpoint, the crystals are converted into the aggregations of the β-spodumene; the specific gravity at 25°,1 C. was now: $d_{4^0} = 2,412$ and the refractive indices about: 1,519.

VI. Spodumene from Maine, U.S.A.; perhaps from *Windham*. This mineral consists of long, opaque, prismatic crystals, looking

Fig. 13.
Dense *α*-Spodumene of Somerö, Finland, ($\times$ Nicols).

like porcelain, with predominant cleavage. The carefully selected material was finely pulverized, and investigated as described before. The specific gravity at $25°,1$ C. was: $d_4° = 3,154 \pm 0,002$; the refractive indices were about: $n_1 = 1,656$ and $n_2 = 1,672$. A microphotograph of it between crossed nicols is reproduced in the fig. 13.

The meltingpoint was determined several times with the thermoelement III; the following results were obtained: 14669 ± 13 M.V., being after correction: $1427° \pm 1°$ C. on the gasthermometer. Also in this case the meltingpoint is not quite so sharp as with the kunzites, just because of the chemical inhomogeneity of the material.

The obtained product had a specific gravity: $d_4° = 2,336$ at $25°,4$ C.; the weakly birefringent, irregularly extinguishing scales, had refractive indices of about: $1,517$ and $1,520$; the birefringence is not greater than: $0,003$.

In fig. 8 a microphotograph between crossed nicols is given of the dense α-spodumene of *Maine*; in fig. 9 the same preparation, molten and solidified into the β-form is reproduced in the same way. The strong analogy with the image of fig. 4, representing an artificial β-spodumene, made from $LiAlO_2$ and LiO_4, is obvious.

Another preparation was not melted, but only kept at a constant temperature of about $1200°$ C. for some hours. The original α-form appeared to be totally converted into β-spodumene; the volume of the mass had increased then in such a degree, that the platinum-

Fig. 8.
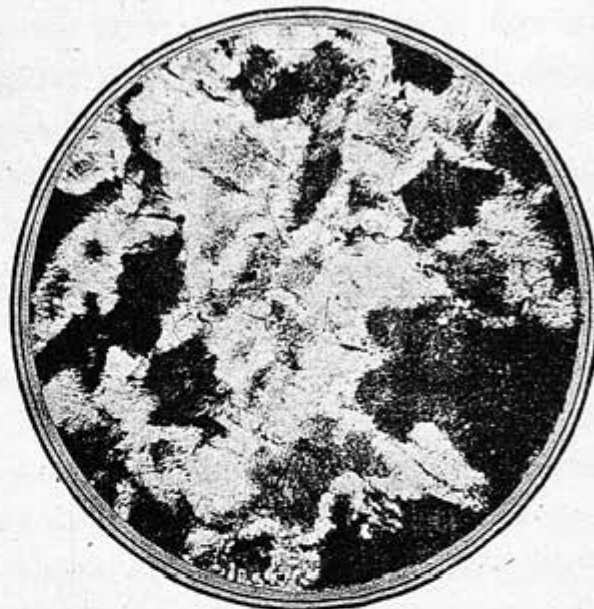Dense α-Spodumene of Maine, between crossed Nicols.

Fig. 9.
β-Spodumene obtained by melting and crystallization of the α-modification ($\times$ Nicols).

crucible was wrecked during the process. The substance showed the typical granular structure of the crystal converted into β-spodumene with undulatory extinction and a mean refractive index of: 1,518. The specific weight at 25°,7 C. was determined to be : $d_{4^0} = 2,309$, and to be 2,317 at 25°,1 C.

§ **13.** In all these experiments it was observed by us, that the platinumcrucibles, in which the silicate was melted and solidified, showed a strong deformation, which increased every time that the experiment was repeated. As fig. 10 shows very clearly, this observed deformation is of such a kind, that it always appears as a *dilatation*, as if the silicate, like water, solidifies under a volume-expansion. The values obtained for the specific volumes. of the crystals and of the *glass*, seem however to make this explanation rather improbable. We have tried by a series of systematic experiments to find out, *when* really this increase of the volume sets in, by measuring the diameter of the crucibles, after their contents had been subjected to different manipulations. In this way, we found, that by far the largest deformation of the crucibles took place, at the transformation of α-, into β-spodumene, which is accompanied by a volume-increase of about 30°/₀. When the substance is then melted once more, and again solidified, the deformation already present will be increased by the thermal expansion of the mass, and because the liquid substance is
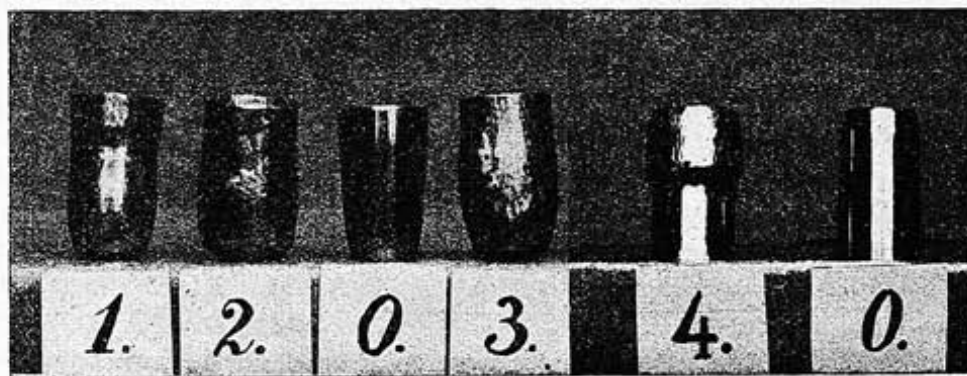

Fig. 10.

Deformation of the platinum crucibles after melting and solidification of the natural Spodumene.

0. Original form of the platinum-crucibles.
1. Pale yellow spodumene of *Minas Geraës, Brasil.*
2. Kunzite of *Sahatany-valley, Madagascar.*
3. Dense Spodumene of *Somerö, Finnland.*
4. Kunzite of *Rincon, California.*

enormously viscous, enclosed air-bubbles are hardly squeezed out, but will rather expand in the mass itself, while the surface of the liquid can change its height only with extreme slowness. In repeating successively the melting and solidifying of the substance a number of times, the deformation-effect will be gradually increased to such an extent that, as fig. 10, N°. 2 shows clearly, at last the crucible bursts. The gradual lowering of the liquid surface in successive experiments can be seen in those crucibles; in such a manner it often happens, that with a strong deformation of the platinum vessels, when they finally look like inflated balloons, the junction of the thermoelement emerges at last out of the surface of the liquid mass, so that the heat-effects on the heating-curves get gradually worse and will finally disappear totally.

§ 14. To control the found meltingpoints, we have made a series of experiments to determine it once more (with the kunzite of Madagascar) by means of the quenching-method, which is to be described afterwards in connection with our experiments for fixing the temperature of beginning transformation. The quenching-system was first calibrated by means of meltingpoint-determinations, made by this statical method with lithiummetasilicate ($1201°$) and diopside ($1391°$); the corrections to be applied to the measured temperatures appeared however to be practically *zero*.

We found in successive experiments :

Kunzite, heated during half an hour at 14600 M.V. and quenched in mercury: All crystallized

„	„	„	„	„	„	„ 14720 M.V. „	„	„	„	: All glass.
„	„	„	„	„	„	„ 14700 M.V. „	„	„	„	: All glass.
„	„	„	„	„	„	„ 14750 M.V. „	„	„	„	: All glass.
„	„	„	„	„	„	„ 14680 M.V. „	„	„	„	: Glass and crystals.
„	„	„	„	„	„	„ 14660 M.V. „	„	„	„	: All crystallized
„	„	„	„	„	„	„ 14690 M.V. „	„	„	„	: All glass.

Thus, the meltingpoint was found to be $1428°$ C. (G. Th.), quite in accordance with the direct meltingpointdeterminations after the dynamical method. In these experiments we once obtained a product after longer heating on 14600 M.V., — just somewhat below the melting-point, — consisting of somewhat larger individuals. They appeared to be large, homogeneously extinguishing plates, whose birefringence was about 0,007, and with refractive indices of 1,513 and 1,519, like those of the β-spodumene, obtained from artificial spodumene after melting and cooling. In convergent polarized light the same inter-ference-image as in the former case, was observed; there can thus

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hardly be any doubt, that the spodumene-modification, which is deposited from the liquid mass, is quite the same as that, which is discerned by us as β-spodumene. There are no reasons to adopt the existence of a third modification, which on cooling should be converted into the β-form, as occasionally has been done.

§ 15. Before describing our experiments with this compound with respect to the study of the transformations into the solid state, the determined values are once more recapitulated in the following table.

From this table (next page) we can see, *that in general the melting-temperatures of the natural kunzites are considerably higher than those for the synthetical products,* and further we can, generally speaking, deduce, that *the meltingpoint of the kunzites are decreasing at the same time with the increase of specific gravity.* (The specific gravities of the two first mentioned kunzites differ too little to give any certain argument for this view). Of the two kinds of dense spodumenes however, the mineral of higher specific density seems to have the higher melting-point also, although in this case the meltingpoints are too close together, and are moreover not sufficiently sharp, to give any certain argument for an eventual rational relation between the two mentioned constants.

§ 16. Now we will proceed to the question, in what relation the different modifications of the compound $LiAlSi_2O_6$ stand with respect to each other. That there are several of these modifications, can already be deduced from the mere fact, *that the product of solidification of the natural spodumenes is quite different from the original substances.*

Our investigations moreover have taught us, that there are really only *two* modifications, which can be discerned as α- and β-spodumene. Of these two forms the β-modification is undoubtedly the one to be considered as the more stable form at temperatures in the immediate vicinity of the meltingpoint. The question, however, then rises immediately: in what relation are α- and β-spodumene to each other? Are they *enantiotropic* forms, like e.g. wollastonite and pseudo-wollastonite? Or are they *monotropic* modifications, as e.g. they are observed in some forms of the pentamorphic magnesiummetasilicate ?

After numerous experiments in this direction, we have come to the opinion that both forms of spodumene must be considered as *monotropic* ones with respect to each other, and *α-spodumene, i.e. all kunzites, hiddenites, spodumenes of nature, must be metastable phases of the compound with respect to the β-form at all temperatures below*

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SYNOPSIS OF THE MELTINGPOINTS AND SPECIFIC GRAVITIES OF NATURAL SPODUMENES.				
Mineral, and Place of Origin:	Specific gravity $d_4\circ$:	Observed E.M.F. of the thermoelement: (intern. M.V.)	Corrected E.M.F.: (Gasthermometer-Elements)	Meltingpoints in ° C. on gasthermometer
Kunzite from *Rincon*, California. (Colourless or pale, lilac, transparent)	3.204 ± 0.003	14683	14675	1428°
Kunzite from *Sahatany-valley* Madagascar (pale rose, transparent)	3.201 ± 0.005	14683	·14675	1428°
Kunzite from *Minas Geräes*, Brasil pale greenish-yellow, transparent)	3.262 ± 0.002	14645	14637	1425°
Hiddenite from *Alexander County*, N. Carolina (emeraldgreen, pale green, transparent)	3.295 ± 0.002	14565	14557	1418°
Dense Spodumene from *Somerö*, Finland (white, opaque, cryptocrystalline)	2.997 ± 0.050	14662 ± 13	14654 ± 13	1426° ± 1°
Dense Spodumene from *Maine*. (Colourless, opaque, macrocrystalline aggregation)	3.154 ± 0.002	14669 ± 13	14661 ± 13	1427° ± 1°

1400 C. Therefore it is neither possible to indicate an "inversion-temperature", below which the α-form, and above which the β-form would represent the more stable phase: at all temperatures below its meltingpoint, the β-spodumene is the only stable form of the compound $LiAlSi_2O_6$. Under what conditions the α-form was always generated in nature, while it was till now *never* obtained in the laboratory from "dry" molten mixtures, may preliminarily be put aside.

The reason however, that the α-modification, once produced, has remained so, notwithstanding its metastability with respect to the β-form, is to be ascribed to the *enormous slowness*, with which the transformation $\alpha \rightarrow \beta$ takes place.

§ 17. To give an idea of this phenomenon, we will describe here a series of experiments, made with the purpose to answer the question, *at what lowest temperature* the transformation $\alpha \rightarrow \beta$-form again will occur with a velocity just observable? Preliminary [1] experiments had taught us that a long and little prominent heat-effect was observed between 900 and 1000° C., if a larger quantity of finely powdered α-spodumene was gradually heated; and the microscopical investigation also taught us soon, that within the mentioned temperature-interval, a transformation is going on with observable velocity. We therefore made the following series of experiments by means of the already mentioned *statical* method For it is evident, that just with reactions proceeding so enormously slowly, *this* method can be used with great success, because *it permits us to keep the studied substances at a constant temperature during an arbitrarily long time*; in this way one can be sure that the reaction is thus completely finished, while the sudden chilling of the preparation in cold mercury will fix the momentaneous state of it in a most effective way.

The following data were obtained by observations with the thermo-element IV; because the thermoelement was *not* placed *in* the mass, but beside it, the whole furnace-system needed to be especially calibrated for this series of experiments.

The calibration of the used quenching-system was executed by means of meltingpoint-determinations after the statical method, with substances, whose meltingpoints in terms of the gasthermometer were

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[1] Vide also : G. Tammann, Krystallisieren und Schmel/en, p, 114. Spodumene $(d=3,17)$ was transformed gradually into a much less dense substance $(d=2,94)$, by heating on a *Bunsenburner* during ten hours. The new product was attacked much more rapidly by HF than the original substance.

already accurately known before. Only in this way is it possible, to find out, what temperature -really corresponds to that, indicated by the thermoelement placed in the furnace. For this purpose we have made use of the meltingpoints of two compounds: Li_2SiO_3 and $LiBoO_2$; the Li_2SiO_3 melts at a temperature of 11956 M. V. on our standard-elements, the second at a temperature, corresponding to an E.M.F. of 7822 M.V. [1]. In this way we observed:

Li_2SiO_3.			$LiBO_2$.	
Heating during a long time at a temperature, at which the E.M.F. of element IV was:	· State of the chilled system:		Heating during a long time at a temperature, at which the E.M.F. of element IV was:	State of the chilled system:
12060 M. V.	All glass.		7800 M. V.	All glass.
12020 „	All glass.		7760 „	All crystals.
11980 „	All glass.		7780 „	Many crystals; a little glass.
11940 „	Much glass, a few crystals		7770 „	All crystals.
11930 „	All crystals		7790 „	All glass.
11950 „	All glass.			
Thus, when the furnace-element indicates 11940 M.V, the meltingpoint of Li-SiO_3 is reached; the correction of the indicated temperatures at 1201°C. to reduce them the nitrogenthermometer, is therefore +16 M.V.			The meltingpoint of the $LiBO_2$ is thus reached, if the furnace-element indicates 7780 M.V.; therefore the correction at 845° C. is: +42 M.V.	

From both these data for 845° C. and for 1201° C., the correction for every intermediate temperature is found by intrapolation; for a temperature of e. g. 965° C., it is +28 M. V.; etc. It is with this number, that the just mentioned temperature (in M. V.) needs to be augmented, to be reduced to the nitrogengasthermometer-scale.

Having in this manner determined the temperature-corrections for the whole quenching-system within the range of temperature from 845° to 1201° C., we have chosen as an object for these experiments

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[1] With the thermoelement IV three series of experiments were made, with heating-rates of 30, 40 and 60 M.V. per half minute. For the lithium-metaborate we found thus successively as mean values: 7786, 7778 and 7781 M.V., — which gives as probable value: 7782 ± 4 M.V. The correction of element IV was +40 M.V. at this temperature; the true meltingpoint thus being at 7822 M.V. = 845 C. (G. Th.).

the *kunzite* of *Madagascar*, and we tried to find in the described way the lowest temperature, at which a just discernible transformation of $\alpha \rightarrow \beta$-form yet occurred. The reader may be put in mind, that the experiments 1—14 were made with a thermoelement, provided with a very thin protecting tube; in the experiment 14—20, this protecting tube was omitted, which appeared however to make no appreciable difference.

No.	Indication of thermoelement IV at the constant temperature of heating ($\pm$ 15 M. V.)		Uncorrected Temp.	Time during which heating lasted	Result of the Chilling:
1		6510 M. V.	723°	2 hours	Only α-modif.; no transformation.
2		6800 ,,	750	2 ,,	idem
3		7380 ,,	805	2 ,,	idem
4		8450 ,,	901	2 ,,	idem
5		9570 ,,	1000	2 ,,	All β-spodumene.
6		9500 ,,	994	2 ,,	idem
7		9070 ,,	957	2 ,,	No transformation; α-modification.
8		9220 ,,	970	2 ,,	idem
9		9360 ,,	982	3 ,,	Partially transform.; α-, and β-form.
10		9170 ,,	966	8 ,,	Probably the same.
11		9280 ,,	975	8 ,,	Partially β-spodumene.
12		9280 ,,	975	15 ,,	All β-spodumene.
13		9260 ,,	973	4 ,,	Probably partially β-form.
14		9260 ,,	973	8 ,,	All β-spodumene.
15		9260 ,,	973	8 ,,	All β-spodumene.
16		9225 ,,	970	8 ,,	For the greater part: β-form.
17	With unprotected thermoelement	9160 ,,	965	4 ,,	All α-spodumene.
18		9200 ,,	968	4 ,,	Evidently partially β-form.
19		9170 ,,	965.5	4 ,,	Some β-modification, many crystals of α-spodumene.
20		9150 ,,	964	4 ,,	No β-form; the transformation has not yet begun.

In this case therefore an evident transformation has already taken place at 9170 M. V. (uncorr.), or at 9198 M. V. = 968° C. (G. Th.).

Similar experiments with the kunzite of *Rincon* taught us, that this temperature is situated somewhat higher, at about 995° C.; in all these cases however, only very long continued heating can lead to a complete transformation of the α-, into the β-form. It is therefore quite evident, that at ordinary temperatures, and even at 400° or 500° C., the transformation-velocity of α-, into β-form must be practically equal to zero; thus the α- and β-spodumenes can be in immediate contact with each other, during an undetermined long time, without transformation taking place.

The transition of α-, into β-form is accompanied by an enormous increase of specific volume: it is augmented from 0.31 to 0.41, being about 33°/₀ of the original value. It often occurred that the heated and transformed powder had risen over the borders of the platinum crucibles. In the described quenching-experiments, the transformation could often be stated already, when the used platinum folium had not yet been opened: it seemed to be inflated by the increase of volume of the enclosed preparation. Microscopically it is observed that the larger crystals of the α-form, in this transformation primarily get innumerable cracks and fissures; afterwards they change into opaque, no longer normally extinguishing aggregations of fine, felty, or even broader needles, whose extinction is *almost* normally orientated on their longer direction; they can be recognized by their weak birefringence, as well as by their low mean refractive index: 1,519. The microphotographs fig. 7 and 9 may give some impression of the aspect of the two modifications between crossed nicols.

§ **18**. It may be expected, that the mentioned transformation-velocity will possibly be affected by some catalysers or by some fluxes in such a way, that it will show a discernible value already at considerably lower temperatures.

Indeed we succeeded in proving, that on heating spodumene-glass with molten sodiumtungstate[1]) at temperatures between 850° and 920° C., after 32 hours a partial crystallization has begun, which however was complete only after 65 hours of heating. The crystal-mass had a refractive index of 1,523, and *appeared to be no other thing than* β-*spodumene*; the determined specific weight was at 25° C.: $d_{4^0} = 2,579$.

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[1]) The great difference between the specific gravities of the silicate and the molten tungstate, makes it necessary to use a platinum stirrer, to bring the silicate from the surface into the molten mass again and again This stirrer was moved by means of a suitable electromotor-driven mechanism.

We then made similar experiments with β-spodumene (of MAINE) in a mixture of $20\,{}^{0}/_{0}\,MoO_3$ and $80{}^{0}/_{0}$ sodiummolybdate at temperatures below 650° C.; on heating during 122 hours on temperatures between 595° and 605° C., we obtained birefringent aggregates of felty needles of the β-modification, with often rectangular borders. The refractive index was 1,527, and while the aggregates of needles did not extinguish in any position between crossed nicols, the rectangular needles often showed a normally orientated extinction. As in the former case, the product had also a pale lilac hue.

Then we made the same experiment with α-spodumene (of *Rincon*); it was heated during 88 hours in the same mixtures at 595° to 605° C. The small pieces of the α-form had got opaque and were converted at their borders or totally into the β-modification; the refractive index was 1,519.

More experiments were made, which all taught us, that from molten magmas, cooled under manifold varied circumstances, never was another thing produced, than either spodumene-"glass", or β-spodumene; however we did not succeed in getting the α-form from dry magmas even a single time. As devitrification of spodumene-glass appears also never to give another phase than β-spodumene, — we are of opinion, that it may be considered as sufficiently proved, that the β-modification is the *only* stable modification below the melting point. The spodumenes of nature therefore *certainly* can*not* be produced from *dry* magmas; they represent metastable forms of the compound, which are very probably generated from circulating solutions, that is by so-called "hydrothermal" synthesis; the natural forms of the compound only appear to be preserved by the enormously retarding factors, which prohibited the transformation into the more stable β-form. Experiments are going on, with a purpose to produce the α-modification of the silicate by such hydrothermal synthesis. The results of these experiments will be discussed in a following paper.

§ 19. Finally we can here give some data, concerning the *lithiumaluminate*: $LiAlO_2$. This compound was prepared by heating in platinum crucibles the weighed, finely ground and well mixed components, — lithiumcarbonate being taken instead of Li_2O, — in our resistance furnaces once at 900° C., then at 1200° C. After the resulting mass had been pulverized, the heating was repeated and these manipulations repeated four times. Analysis of the beautifully crystallized, homogeneous mass gave the following numbers:

	Observed :		Calculated :
Al_2O_3 :	76,8 %	76,9 %	77,3 %
Li_2O :	23,2 %	23,0 %	22,7 %
			100,0

Although a small excess of Li_2O was still present, the substance could be considered as practically pure $LiAlO_2$, — the more so, as on heating, a certain amount of Li_2O always volatilizes gradually. A preparation, heated only shortly at 1600° C. contained, as analysis showed us, only 19,34 % Li_2O and 80,65 % Al_2O_3; no further change had occurred than that the crystals of the original preparation *had got much larger dimensions, while preserving their general properties.* At 1625° C. the substance shows no trace of melting, but decomposes partially, by the volatibility of the Li_2O. The platinum is strongly attacked, Li_2O_2 being formed, and thus the aluminate cannot be heated at higher temperatures, without changing its composition. The meltingpoint can thus be hardly determined; the substance must have been changed a long time before already into Al_2O_3, with perhaps a slight admixture of some lithiumoxide. Even in a "hollow thermoelement", we were not able to melt the substance, notwithstanding it being heated up to 1625° C.

Microscopically the aluminate shows large, round-edged, hexagonal or octogonal plates (fig. 12), with a relatively high birefringence

Fig. 12.
Crystals of *Lithiumaluminate*. (✕ Nicols).

and high interference-colours between crossed nicols. The refractive indices were determined to be: $n_1 = 1,604 \pm 0,001$; $n_2 = 1,615 \pm 0,001$ for sodiumlight; the birefringence was about: 0,012. No axial image could be observed. The specific gravity of the crystals at $25°,1$ C. was: $d_4° = 2,554$.

In a following paper we hope to be able to give an account of the formation and the occurrence of the α-modification of the spodumene in nature, and to review the results so far obtained, also with respect to their geological significance.

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Groningen, May 1914.

Physiology. — "*On the survival of isolated mammalian organs with automatic function.*" By Dr. E. Laqueur. (Communicated by Prof. H. J. Hamburger).

(Communicated in the meeting of April 24, 1914).

When studying the movements of extirpated pieces of gut, I was struck by the following fact: a piece of gut which had contracted for 9 hours in a Tyrode-solution at 37°, to which oxygen had been added, and which had been left to itself at room-temperature, began to move again the next morning, after being heated and after a renewed addition of oxygen. However frequently such experiments with pieces of gut — in the way suggested by Magnus — have been carried out by various investigators, yet the possibility of keeping the gut alive for so long a period seems to be unknown.

Further researches show, however, that the automatic movements of such pieces of gut are of much longer duration than one day and one night. The longest period, as yet observed by me, runs to more than 3 *weeks*. As many as 21 days after the death of the individual the movements of the piece of gut could be observed. This time probably exceeds everything hitherto observed in this respect on mammalian organs working automatically.

We may compare with this, for instance, how long after the death of the individual the heart can be made to contract. The heart is indeed the only automatic organ, as far as I know, on which experiments have been carried out in this direction. Kuliabko, for instance. discovered that when the heart of a rabbit, after being kept for 44 hours after death in an ice-chest, was perfused with Locke's solution, contractions again manifested themselves. The heart