continuance of the discussion in THIS JOURNAL. This reason alone would lead us to decline further controversy on the subject for the present after having had the opportunity of putting our case forward in these pages; another and weightier reason seems now, however, to render further immediate discussion superfluous. During the last year or two a method for the practical determination of crystal structure has been developed by Laue and by W. H. and W. L. Bragg, which gives every promise of ultimately leading to very precise information concerning the arrangement of the atoms in a crystalline structure. While we greatly appreciate the frank and courteous manner in which Professor Richards has dealt with our crystallographic work we think that further discussion on the lines laid down in the preceding two papers may well be postponed until the important developments which are promised have had time to mature.

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THE MIXED CRYSTALS OF AMMONIUM CHLORIDE WITH MANGANESE CHLORIDE.

BY H. W. FOOTE AND BLAIR SAXTON.

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The products which form when mixed solutions of ammonium and manganese chlorides are allowed to crystallize, have been investigated repeatedly and a number of double salts have been described by different investigators.[1] In the early work, the possibility of mixed-crystal formation was not taken into account, so that any material which appeared homogeneous was considered a chemical compound and at least four double salts were described which undoubtedly do not exist. Lehman[2] first recognized that ammonium chloride was capable of forming a curious type of mixed crystal or solid solution with manganese chloride, as well as with a number of chlorides of other metals such as nickel and ferrous and ferric iron, and he and also Johnsen[3] investigated them, chiefly from a crystallographic standpoint. The most complete investigation on the double salts of the chlorides of ammonium and manganese was carried out by Saunders.[4] He repeated the work of some of the previous investigators, following their directions so far as practicable and concluded that only one double salt forms, which has the formula $2NH_4Cl.MnCl_2.2H_2O$. He analyzed a number of products which did not give rational formulas, and concluded that these were mechanical mixtures; but he did not consider the possibility of true mixed-crystal formation. Lehman's work, which appeared nine years previously, was apparently un-

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[1] A summary of the literature on the subject will be found in Abegg's "Handb. der anorg. Chem.," 7th Group, p. 705.

[2] *Z. Kryst.*, 8, 438 (1883).

[3] *N. Jahrb. Min.*, 2, 93 (1903).

[4] *Am. Chem. J.*, 14, 127 (1892).

known to Saunders. The extent of mixed-crystal formation and the conditions which produce mixed crystals instead of double salts have not been determined. While investigating these points, some interesting, and rather unusual, relations have been discovered. Our results show that ammonium chloride and the double salt form two series of mixed crystals, there being a gap between the limiting composition of each type. From the results, conclusions can be drawn as to the components making up the mixed crystals, which has not been possible before.

The method which has been used to determine the solid phases and the conditions for their formation, is essentially the same solubility method that has been used before, by one of us,[1] in determining the mixed crystals of ammonium chloride with nickel and cobalt chlorides. The solubility of varying mixtures of ammonium and manganese chlorides has been determined at 25°, analyzing both residues and solutions. From a series of such results, the solid phases which form can be determined.

Weighed quantities of the recrystallized salts were transferred to bottles, treated with water and warmed till all dissolved. The bottles were rotated for at least 48 hrs. in a thermostat at 25°, using glass rods in the bottles to assist in reaching equilibrium. After the residues had settled in the bottles, weighed portions of solution were drawn off through a filter of glass wool for analysis. The residues were then removed and dried as rapidly as possible between filter papers. Ammonia was determined in the usual manner, by distilling with potassium hydroxide, absorbing the ammonia in standard acid and titrating the excess. Manganese was precipitated as NH_4MnPO_4, filtered on a Gooch crucible and weighed as $Mn_2P_2O_7$. Water was calculated in the residues from the percentage of manganese chloride, assuming that the latter was present as dihydrate. The results for water are practically the same that would be obtained by difference. The analytical data for solutions are undoubtedly somewhat more accurate than for residues. This is because the solution can be obtained free from residue, while the latter is of necessity somewhat contaminated with solution.

The results obtained are given in Table I.

The results are shown graphically in Fig. 1. The percentage of ammonium chloride in the residue is plotted as abscissa and the composition of the solution as ordinate. Two curves are shown, one expressing the composition of the solutions in percentage of ammonium chloride, the other, in percentage of manganese chloride.

Nos. 1–5 in Table I show variable composition of residue and of solution. They are represented in Fig. 1 on the curves AB and CD. In this series, it is evident that mixed crystals of ammonium chloride with varying amounts of manganese chloride dihydrate were present. They correspond

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[1] THIS JOURNAL, 34, 880 (1912).

TABLE I.—SOLUBILITY OF MIXTURES OF AMMONIUM CHLORIDE AND MANGANESE CHLORIDE AT 25°.

	Solution.		Residue.				
No.	% NH_4Cl.	% $MnCl_2$.	% NH_4Cl.	% $MnCl_2$.	% H_2O.	Total.	Residue contains.
1.......	23.97	7.97	93.83	5.31	1.52	100.66	α mixed crystals
2.......	22.94	9.65	90.24	7.76	2.22	100.22	
3.......	21.45	12.31	83.98	12.41	3.55	99.94	
4.......	21.18	13.38	82.03	14.31	4.09	100.43	
5.......	20.10	15.19	76.20	18.60	5.32	100.12	
6.......	19.70	15.92	74.27	20.03	5.73	100.03	α and β mixed crystals
7.......	19.75	16.02	72.74	21.58	6.17	100.49	
8.......	19.69	16.05	70.41	22.93	6.56	99.90	
9.......	19.67	15.47	63.85	28.32	8.11	100.28	
10.......	17.09	18.76	56.18	34.40	9.84	100.42	β mixed crystals or double salt, $2NH_4Cl.MnCl_2.2H_2O$
11.......	15.05	22.44	47.06	41.33	11.83	100.22	
12.......	13.17	24.52	42.81	44.87	12.84	100.52	
13.......	9.15	29.24	39.36	47.64	13.63	100.63	
14.......	5.90	34.78	37.76	48.79	13.96	100.51	
15.......	3.77	39.48	35.66	50.00	14.31	99.97	
16.......	2.98	43.71	16.29	58.27	...	....	Double salt and manganese chloride
17.......	2.94	43.44	7.30	61.88	....	....	

to the mixed crystals with ferric chloride investigated by Roozeboom,[1] van der Kolk[2] and Mohr,[3] and with nickel and cobalt chlorides investigated by one of us.[4] We shall call these crystals the α variety. Nos. 10–15 again show variable composition of residue and solution. They are represented in Fig. 1 on the curves EF and GH. It will be noted, however, that the curves are nearly vertical toward the end, which means that the composition of the residue is nearly constant but has variable solubility. This shows the presence of a double salt. The double salt described by Saunders contains 39.8% NH_4Cl, which is nearly the same as the residue of No. 13, lying on that part of the curve which is nearly vertical. Nos. 14 and 15 contain somewhat more manganese and less ammonium chloride than does the pure double salt. It must be remembered, however, that the residues in determining solubility were of necessity very finely divided, in order to insure equilibrium with the solution, and were, therefore, somewhat contaminated with mother liquor. This accounts for the variation in composition. There seems, therefore, no doubt that the 2 : 1 double salt exists. This series of results, however, gives residues containing up to 64% of ammonium chloride, or about 24% more than the pure double salt, showing that the latter forms a

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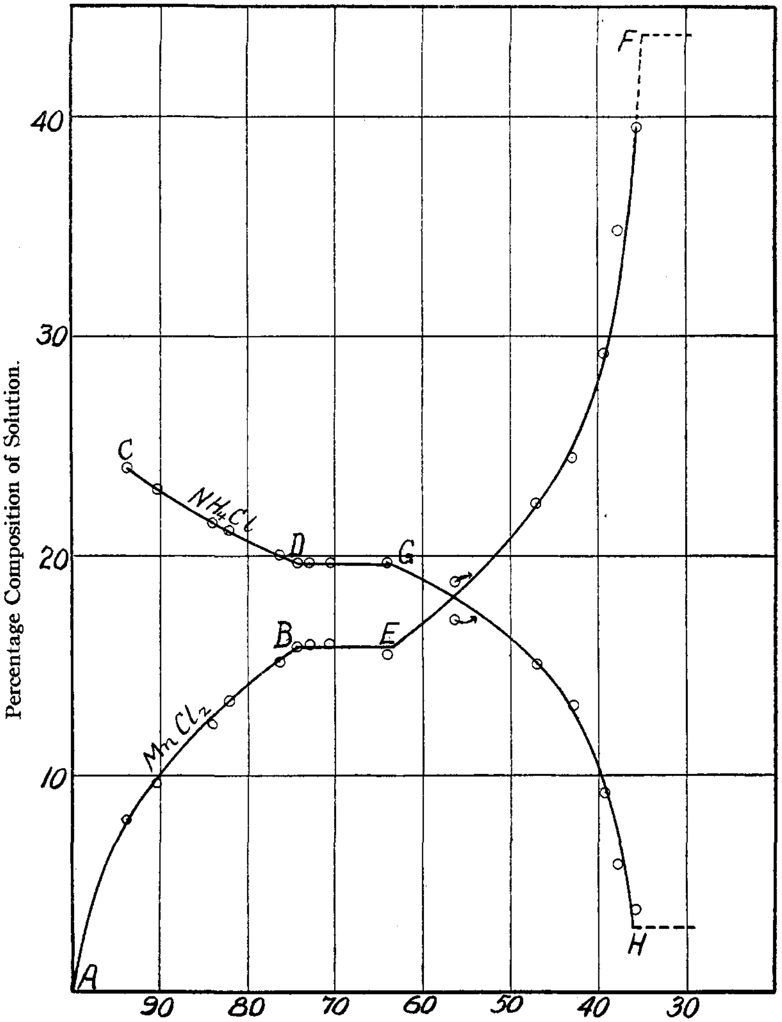
[1] *Z. physik. Chem.*, **10**, 145 (1892).

[2] *Ibid.*, 11, 167 (1893).

[3] *Ibid.*, **27**, 193 (1898).

[4] THIS JOURNAL, **34**, 880 (1912).

series of mixed crystals containing an excess of ammonium chloride. These we have called β crystals. Before the solubility series was completed, there appeared to be a complete series of mixed crystals between ammonium chloride and the double salt. Nos. 6–9 in Table I, represented in the figure by the horizontals, have, however, practically constant



solubility with variable residue, showing that two solid phases were present. In this series, the α and β crystals were evidently both present in variable proportions.

To obtain the pure double salt in well crystallized condition, we prepared a solution whose composition was calculated from our solubility data, such that after 10% of the dissolved salts had crystallized, the remaining solution would have approximately the composition of the solution in No. 13. The amounts used were: 52 g. NH_4Cl; 233 g. $MnCl_2.4H_2O$; and 204 cc. H_2O. The salt separated in good crystals, similar to those obtained by Saunders. It should be mentioned in this connection, that, where either form of mixed crystal was obtained, the material was in a fine granular, poorly crystallized condition, even when it separated slowly from a considerable volume. An analysis of the salt gave the following results:

	I.	II.	Calculated for $2NH_4Cl.MnCl_2.2H_2O$.
NH_4Cl	40.01	40.05	39.80
$MnCl_2$	47.21	46.96	46.81

Another crop of crystals was obtained from a solution which corresponded in composition with that of No. 14 in Table I. The analysis of this crop of crystals was as follows:

	I.	II.
NH_4Cl	39.00	38.99
$MnCl_2$	47.47	47.59

The large excess of manganese chloride in the solution caused some contamination, but the results are sufficiently close to the theory for double salt to prove that it was present.

The results which have been given show that a very rare type of solid solution exists in the present case, in which a single salt and a double salt are each capable of taking up very considerable quantities of the other to form homogeneous mixed crystals. The case is somewhat similar in character to the isomorphism between dolomite and calcite.[1] Nos. 6 and 9 in Table I show the approximate limits in composition of the α and β crystals at 25°.

Calorimetric Results.

In connection with the work on solubility, we have carried out a series of calorimetric determinations which show the heat effect of solid solution. These results confirm the existence of the two types of crystals and also offer very strong evidence regarding the components which make up the mixed crystals.

The method adopted was as follows: The heat of solution of 10 g. of mixed crystals in 500 g. of water was determined. This determination was duplicated in every way except that an equal weight of a mechanical mixture of ammonium chloride and manganese chloride dihydrate was substituted for the mixed crystals. The difference gives the heat involved in the formation of the mixed crystals from the single salts. From these determinations, results which are comparable in different lots of mixed

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[1] *Am. J. Sci.*, 37, 339 (1914).

crystals may readily be calculated. The calorimeter used in the work has been described by Haigh.[1] The silver containing-vessel held about 500 cc. The thermometer used was corrected by comparison with a standard instrument. The total heat capacity of the calorimeter, using 500 g. of water in all the work, was 513.7 calories. The salts were finely ground in every case and dissolved so rapidly that thermometer readings could be taken after an interval of two minutes. The temperature of the water in the outer jacket and in the silver vessel, and the rate of stirring, were so adjusted that radiation corrections were minimized.

For the mechanical mixtures, it was necessary to prepare the dihydrate of manganese chloride, since both the double salt and the mixed crystals contain this component. The method used is that given by Lescoeur[2] and by Dawson and Williams.[3] The method consists essentially in dissolving the tetrahydrate in 95% alcohol and saturating the solution with hydrochloric acid gas. For our purposes, 200 g. of the salt were dissolved in 350 cc. of alcohol. The first yield was about 100 g. of the salt, but more separated later after standing. The product obtained is exceedingly pure. It was dried in a desiccator over caustic potash and finally heated in an air bath at 50° to remove traces of alcohol and acid. To test the purity, manganese was determined as sulfate:

$MnCl_2$ found: 77.66, 77.72; calc. 77.74.

Four samples of mixed crystals were prepared. Two of these were the β crystals, one was the α form and the other (No. 2) prepared before we were aware that two forms existed, was nearly pure α, with probably a slight admixture of the β form. The composition of the solutions from which the samples crystallized was calculated from solubility data, allowing about 10% of the salts dissolved to crystallize. The crystals were small and opaque. Those belonging to the β type had a marked pink color, while the others, with more ammonium chloride, were more nearly white. The following results were obtained by the analysis of each crop.

	NH_4Cl, %.	$MnCl_2$, %.	H_2O, %. (Calculated as dihydrate.)	Total.	Type of crystals.
1	78.55	16.99	4.80	100.34	α
2	75.00	19.78	5.53	100.31	α[4]
3	61.25	29.55	8.46	99.26	β
4	47.96	40.51	11.59	100.06	β

The above results represent, of course, the average composition of each sample. Undoubtedly the first crystals deposited from solution contained somewhat more ammonium chloride. The percentages given were re-

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[1] THIS JOURNAL, **34**, 1144 (1912).

[2] *Ann. chim. phys.*, [7] **2**, 78 (1894).

[3] *Z. physik. Chem.*, **31**, 59 (1899).

[4] Probably contained a small amount of β.

calculated to an even 100% when mechanical mixtures were to be made of the same composition.

The following calorimetric results were obtained, using the mixed crystals whose composition is given above, and mechanical mixtures of the same composition (Tables II–V). The heat capacity of the calorimeter and water, was in all cases 513.7 calories.

TABLE II.

α Mixed Crystals, 78.38% NH_4Cl.

	$t_2—t_1$.	Heat effect (in calories).	Average heat effect (in calories).
1. Mechan. mixture..............	—0.841	—432.1	—432.6
2. Mechan. mixture..............	—0.843	—433.1	
3. Mixed crystals................	—0.815	—418.7	—419.5
4. Mixed crystals................	—0.818	—420.2	

TABLE III.

α Mixed Crystals (chiefly). 74.69% NH_4Cl.

	$t_2—t_1$.	Heat effect (in calories).	Average heat effect (in calories).
1. Mechan. mixture..............	—0.771	—396.1	—394.8
2. Mechan. mixture..............	—0.766	—393.5	
3. Mixed crystals................	—0.755	—387.9	—389.4
4. Mixed crystals................	—0.761	—390.9	

TABLE IV.

β Mixed Crystals. 61.99% NH_4Cl.

	$t_2—t_1$.	Heat effect (in calories).	Average heat effect (in calories).
1. Mechan. mixture..............	—0.472	—242.5	—240.6
2. Mechan. mixture..............	—0.467	—239.9	
3. Mechan. mixture..............	—0.466	—239.4	
4. Mixed crystals................	—0.537	—275.9	—274.9
5. Mixed crystals................	—0.533	—273.8	

TABLE V.

β Mixed Crystals. 47.96% NH_4Cl.

	$t_2—t_1$.	Heat effect (in calories).	Average heat effect (in calories).
1. Mechan. mixture..............	—0.167	— 85.8	— 83.6
2. Mechan. mixture..............	—0.161	— 82.7	
3. Mechan. mixture..............	—0.160	— 82.2	
4. Mixed crystals................	—0.241	—123.8	—121.8
5. Mixed crystals................	—0.233	—119.7	

The actual heat effect caused by the formation of 10 g. of mixed crystals from the single salts is obviously equal to the heat of solution of the mechanical mixture minus that of the mixed crystals. These values are given in Table VI.

TABLE VI.

Heat of Formation of 10.00 g. Mixed Crystals from the Single Salts.

	NH_4Cl in salt. %.	Type of crystal.	Heat effect (in calories).
1...............	78.38	α	—13.1
2...............	74.69	α (chiefly)	— 5.4
3...............	61.99	β	+34.3
4...............	47.96	β	+38.2

There are two conclusions to be drawn from these results without recalculating them in any manner. The heats of formation are small compared with the heats of solution of the salts in water and the heat of formation of the β crystals is positive while that of the α crystals is negative. The small heat of formation is perhaps to be expected, as the few values which have previously been determined on the heat of formation of mixed crystals have all been small. The positive and negative heats of formation offer further evidence that the α and β crystals are of different type.

To recalculate the above results on a gram molecular basis, brings up the question of what components are to be considered in the mixed crystals. The β crystals can hardly be considered otherwise than a solid solution of ammonium chloride in the double salt, but it is evident that the α crystals may be considered as a solid solution, either of the double salt, or of manganese chloride dihydrate, in ammonium chloride. Any thermal calculation based on the double salt requires its heat of formation from the single salts. This has been determined by the method given above, using, as before, 10 g. of material in each determination.

The results obtained are in Table VII.

TABLE VII.—HEAT OF FORMATION OF DOUBLE SALT $2NH_4Cl.MnCl_2.2H_2O$ FROM NH_4Cl AND $MnCl_2.2H_2O$.

	t_2-t_1.	Heat effect (in calories).	Average heat effect.	Molecular heat of formation of double salt.
1. Mechan. mixture	+0.025	+12.8	+15.8	+1084 calories
2. Mechan. mixture	+0.033	+17.0		
3. Mechan. mixture	+0.034	+17.5		
4. Double salt	—0.051	—26.2	—24.5	
5. Double salt	—0.046	—23.6		
6. Double salt	—0.046	—23.6		

From the data we have calculated the heat of combination of 1 gram molecule of double salt with ammonium chloride in the α crystals and of 1 gram molecule of ammonium chloride with the double salt in the β crystals. The results are given in Tables IX and X.

TABLE IX.—HEAT OF COMBINATION OF 1 MOL DOUBLE SALT WITH AMMONIUM CHLORIDE (α CRYSTALS).

	Total per cent. NH_4Cl in mixed crystals.	Mols NH_4Cl: 1 mol double salt.	Heat of combination.
1	78.38	8.97	—2067
2	74.69	6.93	—1427

TABLE X.—HEAT OF COMBINATION OF 1 MOL AMMONIUM CHLORIDE WITH DOUBLE SALT (β CRYSTALS).

	Total per cent. NH_4Cl in mixed crystals.	Mols double salt: 1 mol double salt.	Heat of combination.
3	61.99	0.34	+129
4	47.96	1.26	+133

No. 2 is probably the least accurate, for reasons previously given, and the result is low. Nos. 3 and 4 show nearly constant heat of combination.

In Table XI the thermal results are recalculated to show the heat of combination, assuming that the mixed crystals are merely solid solutions of $MnCl_2.2H_2O$ in ammonium chloride.

TABLE XI.—HEAT OF COMBINATION OF 1 MOL $MnCl_2.2H_2O$ WITH NH_4Cl.

	Per cent. NH_4Cl in mixed crystals.	Heat effect. Cals.
1	78.38	— 981
2	74.69	— 345
3	61.99	+1461
4	47.96	+1189

The results given in Tables IX–XI throw some light on the question which has often been discussed, as to how these mixed crystals, and others of similar type, are to be regarded. Previously, only the α type of crystals has been investigated and there has been no means of deciding whether the component in solid solution was the chloride of the polyvalent metal or a double salt of the latter with ammonium chloride. Without means of deciding, the simplest method of representing the facts has been to regard the crystals as solid solutions of the single salt in ammonium chloride. The heats of combination or solid solution given in Tables IX and X, assuming that the components are ammonium chloride and double salt, are at least approximately constant for each type of crystal, a regularity which is comparable with the nearly constant heat of solution of a salt in water with varying dilution. As will be shown in the article which follows, the heat of solid solution in a simple case of isomorphism is also very nearly constant, independent of dilution. Assuming that mixed crystals of ammonium chloride and manganese chloride form, Table XI, there is no constancy or regularity evident. The evidence, it seems to us, shows that the double salt is present in both types of mixed crystals. The fact also that the double salt can take up ammonium chloride (β crystals) makes it fair to assume that the reciprocal relation exists of the double salt in ammonium chloride (α crystals).

The α crystals are similar in solubility relations to the mixed crystals with nickel and cobalt chlorides, although no corresponding double salts form in pure condition. These should undoubtedly be regarded as belonging to the same type, containing the unstable double salts $2NH_4Cl.NiCl_2.2H_2O$ or $2NH_4Cl.CoCl_2.2H_2O$ in ammonium chloride.

It may be worth while to point out that there are other cases of solid solution between dissimilar substances, where there is uncertainty as to the components. For instance, pyrrhotite may be regarded as a solid solution of pyrite or of sulfur in ferrous sulfide; a hardened steel may be considered as a solid solution of iron carbide or of carbon in iron, and nephelite, as it occurs in nature, as a solid solution of albite or of silica in the compound $NaAlSiO_4$. Analogy with the case investigated suggests that the components in these instances are iron sulfide and pyrite, iron and iron carbide and nephelite and albite. Further investigation is needed, however, to decide these points.

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ON THE HEAT OF FORMATION OF SOLID SOLUTIONS.

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Ever since van't Hoff pointed out that isomorphous mixtures could be considered as solid solutions, the problem has been an interesting one as to what extent the properties of such mixtures are a linear function of composition. It is safe to say that, in general, the properties are much more nearly linear than are the properties of liquid solutions. For instance, probably no isomorphous mixtures diverge as widely in properties from a linear relation as solutions of water and nitric acid. This is because substances which are isomorphous are usually very closely related chemically, while liquids which are totally unrelated may dissolve each other readily. Some properties are so nearly linear that it has not been possible to measure any difference. Retgers has shown, for example, that the specific gravity of isomorphous mixtures is in general what would be calculated if they were considered as mechanical mixtures. This property, however, cannot be measured with very great accuracy and it is probable that a difference does exist but that it is small. Melting points and vapor pressures, so far as they are known, commonly show small variations from the linear relation. These small variations in properties are an expression of the fact that isomorphous mixtures contain a somewhat different amount of energy than mechanical mixtures of the same composition do and that isomorphous mixtures have what may be termed a heat of solid solution which, in general, is small. Ostwald[1] demonstrated this in a few cases before van't Hoff's work appeared, and the same has been shown since, notably by Sommerfeldt,[2] Beketoff,[3] Kurnakov and Zemcynznyj[4] and Wrzesnewski.[5] The results all show that there is a small positive or negative heat of formation.

Salts which are isomorphous with each other only to a limited extent are in some ways comparable with partially miscible liquids. The composition of each solid, when it has become saturated with the other, is a function of the temperature, as it is with liquids. With liquids, however,

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[1] *J. prakt. Chem.*, 25, 1 (1882).

[2] *Jahrb. Mineral.*, Beibl., 13, 435 (1899–1901).

[3] *Z. anorg. Chem.*, 40, 355 (1904).

[4] *Ibid.*, 52, 186 (1907).

[5] *J. Russ. Phys. Chem. Soc.*, 43, 1364 (1911).