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Non-solvated aluminum hydride. Crystallization from diethyl ether—benzene solutions

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Crystallization of non-solvated aluminum hydride from a diethyl ether—benzene mixed solvent was studied. The desolvation of $AlH_3 \cdot (Et_2O)_x$ etherate in solution and the crystallization of α-AlH_3 during polythermal heating of the solution occur only in the presence of ≥10 wt.% $LiAlH_4$. The process is multistage, and the crystallization begins with the formation of the $AlH_3 \cdot 0.25Et_2O$ solvate, which recrystallizes in the solid phase into γ-AlH_3 and then α-AlH_3. Four crystalline modifications of aluminum hydride were characterized by X-ray diffraction and electron microscopy.

Key words: aluminum hydride, alanes, etherates, synthesis, phase transitions, crystalline modifications.

The development of fuel cells using hydrogen as a combustible component requires search for economical and convenient methods for obtaining and storing this gas. It is most convenient to store hydrogen bound into hydrides. Among the latter, non-solvated aluminum hydride alane is the best in terms of hydrogen weight content and volumetric density, decomposition temperature, and safety.

Alane in the form of adducts with various donor molecules with the composition $AlH_3 \cdot nL$ (L designates tertiary amines, ethers, phosphines, *etc.*) has been known since the 1940s.[1] However, although all these substances are aluminum hydride derivatives, they are inappropriate as a hydrogen source for several reasons, first of all, because of the low percentage of "active" hydrogen and high fire risk.

The first perfect procedure for the synthesis of pure (non-solvated, *i.e.*, containing no donor molecules) alane was described in Ref. 2. The method proposed for the synthesis is the crystallization of aluminum hydride from an ether—benzene mixed solvent in the presence of 10—20 wt.% $LiAlH_4$ and (sometimes) the same amount of $LiBH_4$. Rhombohedral (hexagonal) α-AlH_3 is formed with solvent distillation, decreasing the weight fraction of ether and increasing the temperature of the solution. In addition to α-AlH_3, several other modifications of non-solvated alane (α', γ, ε, δ, and ξ) were obtained.[2] These substances are formed upon both crystallization from solution and heating *in vacuo* of a fine dry mixture of aluminum hydride etherate with lithium tetrahydridoaluminate. Unlike adducts, the substances obtained react unreadily under normal conditions with atmospheric oxygen, acids, and water, but vigorously interact with alkalis, as aluminum metal does.

Up to recent time, of the six modifications described in Ref. 2 only the structure of one of them, namely, the rhombohedral (hexagonal) α-phase, has been known.[3] Perhaps, this is caused by both difficulties in the isolation of phases other than α-AlH_3 in the pure state and the absence of practical interest from the scientific society. Despite all attempts, all prepared samples contain[2] some amounts of other alane modifications as admixtures. The structural data for γ- and δ-AlH_3 have recently been published.[3] As has been assumed,[6] all of them are inorganic polymers, whose simplest structural units, *viz.*, $\{AlH_6\}$ octahedra, are cross-linked in a way other than in the case of the α-phase.

Since all aluminum hydride phases are isolated, as a rule, from solutions, in the present work we studied their formation during crystallization from a diethyl ether—benzene mixed solvent.

Experimental

All procedures involved in the purification, preparation, and storage of the starting substances, the preparation of aluminum hydride solutions, crystallization, and treatment of the crystallization products (washing, drying, packaging) were carried out

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under dry argon in a dry box or *in vacuo* using Schlenk techniques.

Benzene, toluene, and octane were purified using standard procedures and were dried over $LiAlH_4$ prior to use. After drying and distillation from alkali, diethyl ether was treated with sodium benzophenone ketyl, distilled under argon, refluxed over $LiAlH_4$, and distilled again. The final procedure of ether preparation was the dissolution of aluminum chloride in the ether and solvent redistillation.

Since the desolvation mechanism and the stability of non-solvated hydride depend very strongly on the quality of the starting substances and, primarily, on admixtures of compounds of transition metals (such as titanium, iron, and chromium) even in concentrations $<10^{-3}$ wt.%, all crystalline starting substances and apparatus were thoroughly purified and cleaned, respectively.

Commercial $LiAlH_4$ was recrystallized from an ether—toluene (1 : 1, concentration ~30 g L^{-1}) mixture. For this purpose, alanate was dissolved at 35—40 °C, the undissolved solid was filtered off, and the solvent was removed from the transparent solution by heating in an oil bath. The process ceased when the temperature in the flask approached 95—98 °C. The suspension was cooled down, and the precipitate was separated from the mother liquor on a special frit funnel, washed with pentane, and dried *in vacuo* with slight heating. Thus obtained $LiAlH_4$ crystallizes as prisms up to 1.5 mm in length, raises no dust, has lower fire risk, and is soluble in diethyl ether up to 98—99%.

Commercial $AlCl_3$ was subjected to double sublimation from the melt over aluminum metal shavings. The mixture was placed in a Pyrex tube (≤5 vol.%), which was vacuumized using a fore pump, sealed off, placed into a tubular furnace to 4/5 of the tube length, and heated to 200—220 °C. The sublimate was condensed on a cooler part of the tube. It was soluble in diethyl ether.

A solution of alane with an AlH_3 concentration of 3—5 g L^{-1} was prepared *via* the Schlesinger reaction[7]

$$3\ LiAlH_4 + AlCl_3 \cdot x Et_2O \xrightarrow{Et_2O—C_6H_6}$$

$$\longrightarrow 4\ AlH_3 \cdot x\ Et_2O + 3\ LiCl$$

by mixing a solution of $AlCl_3$ (50 mL) in a diethyl ether—benzene (1 : 1.5) mixed solvent (in some experiments, *n*-octane was used as the second component) containing 1.5—2.5 g of the substance, with a solution of $LiAlH_4$ (550 mL) in the same solvent containing lithium tetrahydridoaluminate (1.5—2.5 g, 10—15% stoichiometric excess). The solution with the precipitate was stirred for 20—25 min, and the precipitate was then let to settle down and decanted. The flask with the transparent solution was placed in an oil bath heated to 110 °C and was kept in the bath with continuously distilling off the solvent until the onset of the crystallization (74—76 °C). From the moment of crystallization, the suspension (40—50 mL) was taken at an interval of 15—20 s from the flask into a frit funnel. The solid phase was immediately separated from the mother liquor, dried in a low vacuum, and transferred into tubes. Thus prepared samples, five to eight in number, were taken from one reactor in one entry.

In particular entries, aluminum hydride etherate was synthesized using $NaAlH_4$. In this case, the synthesis was carried out in special reactors equipped with high-speed (cavitation-type) stirrers, whose design has been described.[8] However, when using these solutions for the synthesis of the non-solvated substance, 10—15 wt.% $LiAlH_4$ were introduced into the solutions, because in the absence of this admixture only the $AlH_3 \cdot 0.31Et_2O$ solvate was obtained.

The powder X-ray diffraction analysis of the samples obtained, which were placed in sealed in vacuum-sealed glass capillaries together with a standard (silicon powder), was carried out on a Guinier G670 HUBER diffractometer. Diffraction patterns were indexed using the WinXpow (Stoe) program package followed by parameter refinement by the least-squares method. Thermal analysis was carried out on a Q1500D system at a heating rate of 10 °C min^{-1}. Electron microscopic examinations were carried out using a JSM 100C instrument.

The thermobaric studies have been described earlier.[9]

Results and Discussion

The crystallization of aluminum hydride from a diethyl ether—benzene solution starts (depending on the concentration of the solution, the amount of $LiAlH_4$ taken over the stoichiometric amount for the Schlesinger reaction, and the amount of ether in the mixed solvent) in the temperature interval 74—76 °C to form semitransparent spherulites 0.8—1.5 mm in diameter, which inflamed immediately on contact with water. According to the elemental analysis data, the substance composition approaches to the formula $AlH_3 \cdot 0.25Et_2O$ (let us name it "pre-hydride"). Since at this temperature $LiAlH_4$ begins to crystallize simultaneously with the solvate, 2 to 6% alanate (according to X-ray powder diffraction and elemental analysis data) are observed in the etherate as an impurity. The formation of a solvate (without indication of its composition) mixed with $LiAlH_4$ has been observed previously.[2] At the same time, an etherate of analogous composition, to which the formula $Al(AlH_4)_3 \cdot Et_2O$ was ascribed, was described in more detail.[10—12] However, its physicochemical properties differ radically from those of the solvate isolated by us.

The diffraction data obtained for "pre-hydride" are given in Table 1 in comparison with the characteristics of the solvate of composition $AlH_3 \cdot 0.31Et_2O$ most frequently mentioned in literature, which was figuratively named[13] "dead" (most likely, due to its "unwillingness" to turn into the non-solvated hydride upon thermal treatment; however, it reacts vigorously with water causing ignition as all compounds of this type do), and "aluminum alumohydride monoetherate." [11] The last two substances were synthesized as the products of the Schlesinger reaction carried out with the strictly stoichiometric ratio of the reactants with subsequent concentrating by evaporation of the ethereal solution and drying of the residue *in vacuo*.

As can be seen from the data in Table 1, these etherates have no common features from the viewpoint of X-ray diffraction. The latter two crystallize[10,13] in cubic lattices (no indexing is presented), while "pre-hydride" is a crys-

Table 1. X-ray diffraction data for aluminum hydride etherates

$AlH_3 \cdot 0.25Et_2O$ ("pre-hydride")					$AlH_3 \cdot 0.31Et_2O$ [13]		$Al(AlH_4)_3 \cdot Et_2O$ [10]	
d/Å	I_{rel} (%)	$1/d_{exp}^2 \cdot 10^4$	hkl	$1/d_{calc}^2 \cdot 10^4$	d/Å	I_{rel} (%)	d/Å	I_{rel} (%)
12.01	100	69	001	68.5	12.0	100	11.777	100
4.62	70	469	200	469	6.10	60	6.804	5
4.42	15	512	112	516	5.05	40	6.320	10
4.23	30	559	020	558	—	—	4.601	60
4.02	20	619	003	619	—	—	—	—
3.86	20	671	120	665	3.85	40	—	—
3.80	40	691	202	682	—	—	—	—
3.56	30	788	212	821	—	—	—	—
			013	756	—	—	—	—
3.17	5	995	301	987	—	—	3.263	50
3.10	10	1038	221	1034	—	—	—	—
2.88	40	1203	104	1198	3.03	40	2.882	40
2.80	30	1266	030	1266	—	—	—	—
2.65	5	1429	131	1436	—	—	—	—
2.61	5	1468	320	1476	—	—	2.561	15
2.42	10	1713	005	1712	—	—	2.307	7
2.35	15	1809	105	1814	—	—	1.941	6

talline product and its diffraction pattern is indexed in the tetrahedral lattice with the parameters $a = 9.90$, $b = 8.54$, and $c = 12.05$ (±0.01) Å. However, since the IR spectra of all solid etherates, including "pre-hydride," in the region of stretching and bending vibrations of the Al—H bond are similar, it can be assumed that their structures are also similar. It is most likely that the main elements of their structure, as in the non-solvated hydrides, are the $\{AlH_6\}$ octahedra, in which some hydride atoms are replaced with an ether molecule and the differences are caused by distortions in the regularity of octahedra cross-linking into the inorganic polymer.

Nevertheless, this is sufficient for the thermal behavior of the etherates and "pre-hydride" to be substantially different. The thermoanalytical curves of the decomposition of the etherates synthesized by different methods but studied under the same conditions are presented in Figs 1—3.

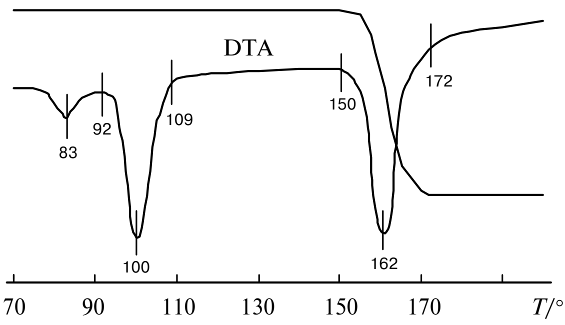

Fig. 1. Thermoanalytical traces of the decomposition of the $AlH_3 \cdot 0.25Et_2O$ etherate ("pre-hydride").

Figure 1 illustrates the thermal decomposition of the "pre-hydride." It is seen that the etherate decomposes in three endothermic stages. At the first stage, in the temperature interval 75—95 °C the substance is desolvated in part to the molecular composition $AlH_3 \cdot (0.05—0.08)Et_2O$ (elemental analysis and GLC data). The diffraction pat-

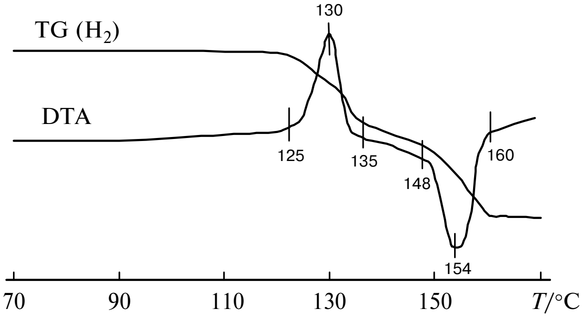

Fig. 2. Thermoanalytical traces of the decomposition of the $AlH_3 \cdot 0.31Et_2O$ and $Al(AlH_4)_3 \cdot Et_2O$ etherates.

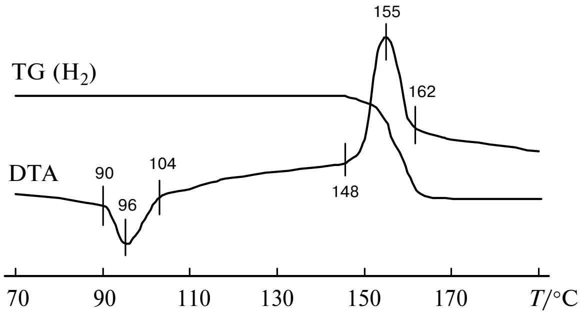

Fig. 3. Thermoanalytical traces of the decomposition of an $AlH_3 \cdot 0.31Et_2O + LiAlH_4$ (15 wt.%) mixture.

tern of the residue shows γ-AlH_3 and some amount of the amorphous phase (halo at small angles). In the temperature interval 100—105 °C, the ether is released completely and most of the γ-AlH_3 is transformed into α-AlH_3, which decomposes at 160—165 °C. According to the X-ray diffraction data, the residue contains only the aluminum metal phase.

The decomposition of the solvates synthesized by earlier described procedures**[11—14]** takes place in a similar way (see Fig. 2): exotherm at 130—135 °C coinciding with the onset of hydrogen evolution, which is almost immediately transformed into the endotherm at 150—155 °C, and complete hydrogen evolution after the end of the endotherm. After decomposition the residue contains the aluminum metal phase and a minor amount of alumina (corundum, after heating of the sample to 550 °C).

The unexpectedly strong dependence of the properties of the etherates on the ether content attracts attention. At first glance, the difference of 0.06 *M* of ether between the "dead" solvate $AlH_3 \cdot 0.31Et_2O$ and the "pre-hydride" $AlH_3 \cdot 0.25Et_2O$ is insignificant, but this change in the composition is accompanied by drastic changes in the properties of these substances. Therefore, it is not surprising that numerous and very contradictory data concerning both the synthesis of alane and the synthesis and properties of the etherates themselves were published.

The character of decomposition of solvates of this type remains virtually unchanged, and they are synthesized with 5—8% deficiency or 5—8% excess $LiAlH_4$ compared to the stoichiometry of the Schlesinger reaction. However, if at least 15% $LiAlH_4$ (or an equivalent amount of LiH, which can turn into alumohydride under thermolysis conditions) are added to the dry etherate $AlH_3 \cdot 0.31Et_2O$ and the mixture is ground in an agathe mortar or a ball mill for 15—20 min, the decomposition thermoanalytical curves and the composition of the resulting intermediate and final products change. Under these conditions, during heating at the first endothermic stage at 90—100 °C (see Fig. 3) the etherate is partially desolvated and a mixture of γ-AlH_3 and $AlH_3 \cdot (0.11—0.14)Et_2O$ amorphous to X-ray with the component ratio ~1 : 2 is formed. This mixture also decomposes at 150—160 °C but exothermically. It is most likely that the relatively large amount of oxygen in it (in the ether moiety) is sufficient to initiate the oxidation of the non-solvated product and to change the sign of the thermoanalytical feature. This assumption is indirectly confirmed by the appearance of the thermolysis residue, which is not a friable powder as in the case of the "prehydride" but a black-brown "spongy" fusion cake.

The ratio of the solvated (amorphous to X-rays) and non-solvated (crystalline) components in the mixture can be changed toward the latter by prolonged isothermal heating *in vacuo* and/or by an increase in the mole fraction of $LiAlH_4$. However, in any case, the properties of thus obtained γ-AlH_3 differ appreciably from the properties of the product isolated by crystallization from solution. Fine-particle γ-AlH_3 resulting from the solid-phase transformation is very unstable, easily oxidizable, and solvatable by diethyl ether; reacts vigorously with dilute acids; and gradually transforms on storage into the α-modification even at ambient temperature.

Thus, our studies confirm completely the earlier conclusions**[2]** about the desolvating role of $LiAlH_4$ for the synthesis of alane from its etherate and about the minimum amount of this substance necessary for desolvation.

The next stage of crystallization detected by macromethods during polythermal heating of the solution is associated with the disappearance of the spherulites, which are recrystallized almost immediately with a 0.5—1.0 °C increase in the solution temperature. The appearance of γ-AlH_3 as needles with split ends is observed in the precipitate both visually and by the X-ray diffraction method (Fig. 4, *a*). Almost simultaneously fine crystals of α-AlH_3 appear on the surface of the needles (Fig. 4, *b*, *c*). They grow rapidly to a size of 10—35 μm but still remain wrapped with particles of the needle-like γ-phase (Fig. 4, *d*). At the end of the process (in 10—15 min when the solvent temperature increases to 76—77 °C), γ-AlH_3 disappears almost completely (Fig. 4, *e*), but particular "needles" of the α′-phase (in the center of the ellipse in Fig. 4, *e*) are sometimes observed in the bulk of α-AlH_3 crystals.

The introduction of lithium borohydride approximately in the same amounts as $LiAlH_4$ into a solution of aluminum hydride etherate (the same approach was proposed in Ref. 2) does not favor desolvation but makes all stages of the process more pronounced and increases the yield of the non-solvated substance, the degree of crystallinity of all intermediate products, and the thermal stability of the resulting alane. When solutions, in which the ratio of three major components $LiAlH_4$, $LiBH_4$, and AlH_3 (2 : 1 : 2—2 : 1 : 3) corresponds to the compositions of the $\{2LiAlH_4 \cdot AlH_3 \cdot 4Et_2O\}$ and $\{LiBH_4 \cdot 2AlH_3 \cdot 3Et_2O\}$ complexes formed in the $LiAlH_4—AlH_3—Et_2O$ and $LiBH_4—AlH_3—Et_2O$ systems, are used, the α-AlH_3 crystals obtained**[14]** differ from the "standard" crystals synthesized with 15% additives of $LiAlH_4$ and $LiBH_4$ by both their shape (cubes of similar sizes with the smooth surface (Fig. 4, *f*)) and very high thermal stability and purity. The crystallization rate of α-AlH_3 in this method is so high that, most likely, all intermediate stages cannot be observed by the sampling method.

At the moderate rate of transformations usually observed for hydride crystallization from etherate solutions with the AlH_3 concentration 2—6 g L^{-1} and 15% excess $LiAlH_4$, the composition of the distilled-off solvent passes through two or three maxima depending on the etherate concentration rather than changing monotonically as in

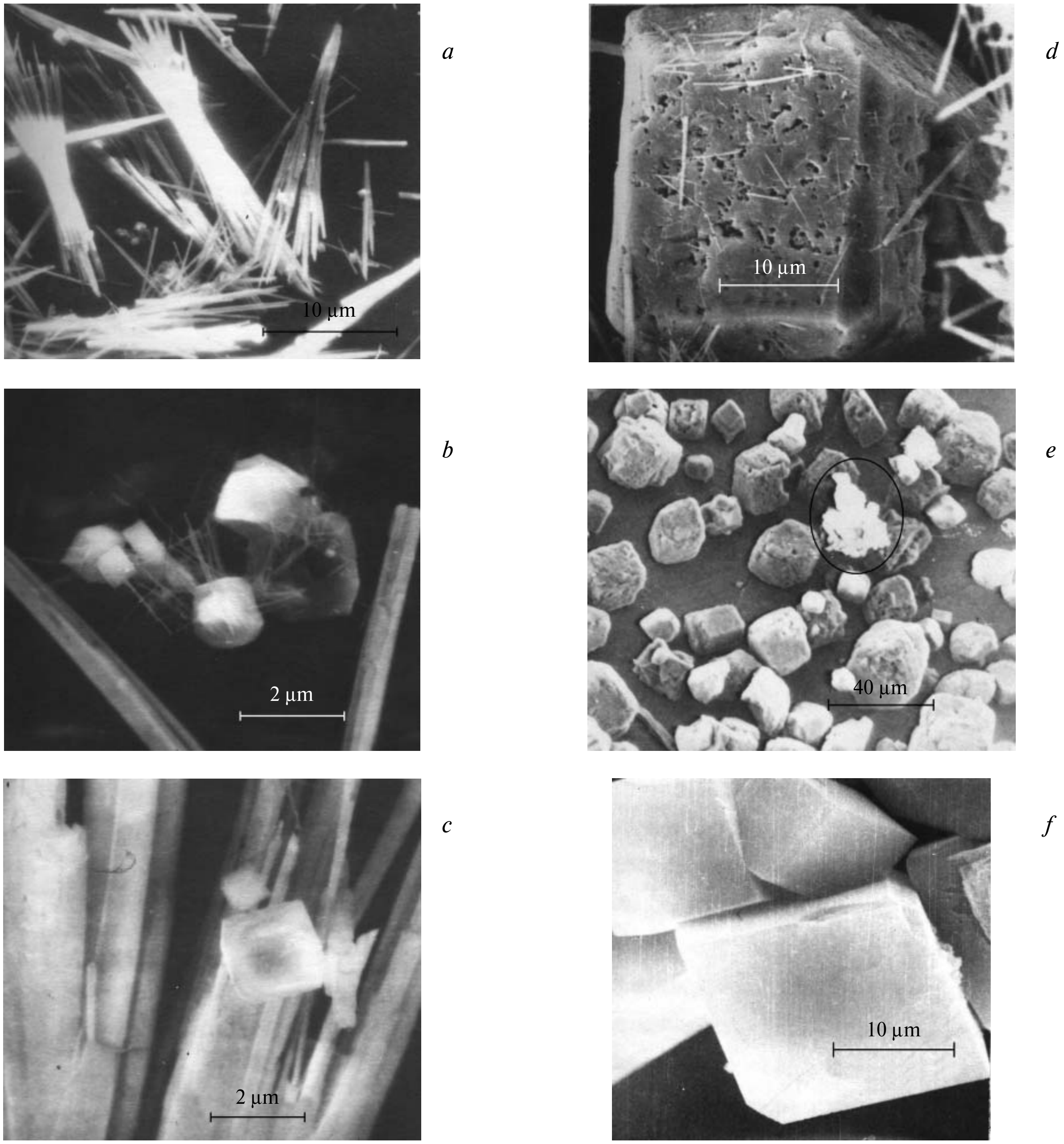

Fig. 4. Phase composition changes upon the polythermal crystallization of aluminum hydride under standard conditions (*a*—*e*) and the crystal shape in the α-phase upon crystallization from solutions with the ratio $LiAlH_4 : LiBH_4 : AlH_3 = 2 : 1 : 2$ (*f*).

the pure ether—benzene system. These changes coincide in time and temperature with the above-described processes of etherate desolvation. As can be seen from the data in Fig. 5, the first, diffused maximum is observed immediately before the solid phase formation and is not related to any visible changes in the solution. Perhaps, its appearance is caused by the pre-crystallization of etherate molecules accompanied by the loss of a portion of ether, but this phenomenon can be ascribed to other factors. The beginning of the second peak coincides in time and temperature with the vigorous boiling up of the solution, opalescence, and the formation of flakes, from which spherulites or "pre-hydride" are formed very rapidly. This peak is not always manifested (see Fig. 5): upon hydride crystallization from dilute solutions (<2 g L^{-1}) it disappears and, most likely, merges with the third maximum. The appearance of the latter coincides in time with spherulite crystallization and with the settling of the denser γ-phase on the bottom of the reactor. It is seen that two most intense maxima shift toward higher temperatures

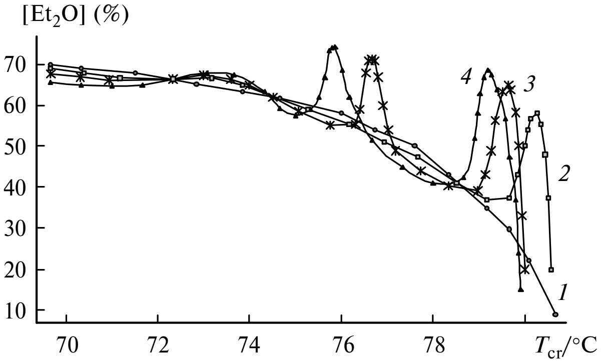

Fig. 5. Change in the Et$_2$O percentage in the gas phase during crystallization in the absence (*1*) and presence of aluminum hydride in the concentration 2.0 (*2*), 3.7 (*3*), and 6.0 g L^{-1} (*4*).

with a decrease in the concentration of the solution, which is quite natural.

When the desolvation is carried out in an isothermic regime, in which an etherate solution is fed into the reactor with the pure solvent heated to 76—77 °C, on the one hand, alane crystallization is somewhat easier and, on the other hand, becomes more complicated. At the initial state of solid phase formation, no stage of spherulite formation is observed. However, this does not mean that the spherulites are not formed at all. In this case, most likely, the rates of their formation and recrystallization are so high that they cannot be taken quickly from the reactor and kept. At the same time, even the first portions of crystals contain two (γ, α′) or three (γ, α′, α) phases, the quantitative ratio between which depends on the crystallization duration (Fig. 6). It is most likely that the α-phase appears not immediately but some time after the formation of alane crystals in the form of the γ- and α′-phases. Since sampling from the reactor requires some time for preparation, this time can be enough for the partial or even complete conversion of the γ- and α′-phases into α-AlH$_3$. As can be seen from the data in Fig. 6, in the reactor only the hexagonal modification is usually observed 15—25 min after the crystallization onset in the reactor. The use of a solution of complexes as the initial one imparts specific features to the isothermal crystallization method. As in the above case, even the first portions of the resulting solid phase contain only α-AlH$_3$ crystals with cubic habitus and appreciable amounts of crystalline LiAlH$_4$ and LiBH$_4$.

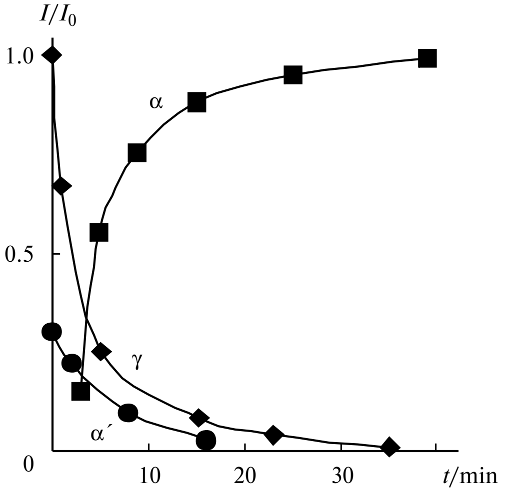

Fig. 6. Change in the proportions of the AlH$_3$ α-, α′-, and γ-phases during crystallization (according to the X-ray diffraction data).

It should be mentioned that, as the authors of Ref. 2, we achieved the formation of absolutely pure single-phase samples except for α-AlH$_3$ in none of the cases of alane crystallization from solution. Moreover, out of the whole described[2] diversity we distinguished only four phases mentioned in Ref. 6. The X-ray diffraction data and indexing results for these phases are given in Tables 2 and 3, and the general view of the phases is shown in Fig. 7. In the framework of the synthesis method used, cubic β-AlH$_3$ appeared occasionally in the crystallization products, always as a mixture with other phases, and reasons for its formation and stabilization remained unclear. This modification differs from the other modification isolated from solution by the absence of any pronounced cutting and a very small particle size (<1 μm), *i.e.*, the complete absence of visual differences. This is the reason for the absence of its microphotograph. The other phases are easily identifiable even with a simple optical microscope. The shape of the α′-phase crystallizing as a carnation bud is especially characteristic, which is seen in Fig. 4, *e*.

Nevertheless, among the four aluminum hydride modifications obtained by us, the β-phase has one property that distinguishes it from the γ- and α′-phases: it does not transform into α-hydride on simple heating, as it is observed for other less dense modifications. However, at pressures below 5 GPa and temperatures 100—150 °C, all phases, including the β-phase, undergo the phase transition to α-AlH$_3$. In this case, no other more dense aluminum hydride modifications are observed under pressures

Table 2. Unit cell parameters (±0.01 Å) and the symmetry type of the aluminum hydride phases obtained by crystallization from solutions

Modification	*a*	*b*	*c*	*Z*	ρ*/g cm^{-3}	
		Å			I	II
Rhombohedral (hexagonal) α	4.45		11.80	6	1.47	1.45
Orthorhombic γ	5.34	7.33	5.80	6	1.31	1.30
Orthorhombic α′	6.62	6.48	5.62	6	1.24	1.22
Cubic β	9.04	—	—	16	1.22	—**

* I is calculation, II is experiment.

** A mixture with α-AlH$_3$ is formed.

Table 3. Results of indexing the diffraction patterns of the α′- and β-phases of aluminum hydride

α′-AlH$_3$					β-AlH$_3$				
d/Å	I_{rel} (%)	$1/d_{exp}^2 \cdot 10^4$	hkl	$1/d_{calc}^2 \cdot 10^4$	d/Å	I_{rel} (%)	$1/d_{exp}^2 \cdot 10^4$	hkl	$1/d_{calc}^2 \cdot 10^4$
5.63	100	315	001	316	5.235	100	365	111	365
3.30	80	917	200	918	3.731	80	1341	311	1341
3.23	10	956	020	952	2.617	80	1460	222	1462
2.845	40	1235	210	1230	2.520	10	1575	320	1580
2.810	80	1266	002 021	1266	2.260	60	1960	400	1950
2.314	40	1868	220	1870	2.195	10	2076	410	2072
2.138	60	2188	202 221	2185	2.130	10	2204	330	2194
1.964	15	2594	311	2608	2.080	40	2311	331	3216
1.785	10	3139	222	3136	1.742	40	3295	333 511	3291
1.650	15	3673	400	3674	1.604	40	3887	440	3901
1.621	10	3806	040	3806	1.531	40	4266	531	4266
1.582	12	3996	401	3990	1.418	20	4973	443	4998
1.558	10	4120	123	4116	1.365	20	5367	622	5363
1.456	10	4717	240	4724	1.269	20	6210	551 711	6217
1.423	10	4938	402	4940	—		—	—	—
1.405	8	5066	004	5064	—		—	—	—
1.293	8	5981	204	5982	—		—	—	—
1.265	6	6249	124	6246	—		—	—	—

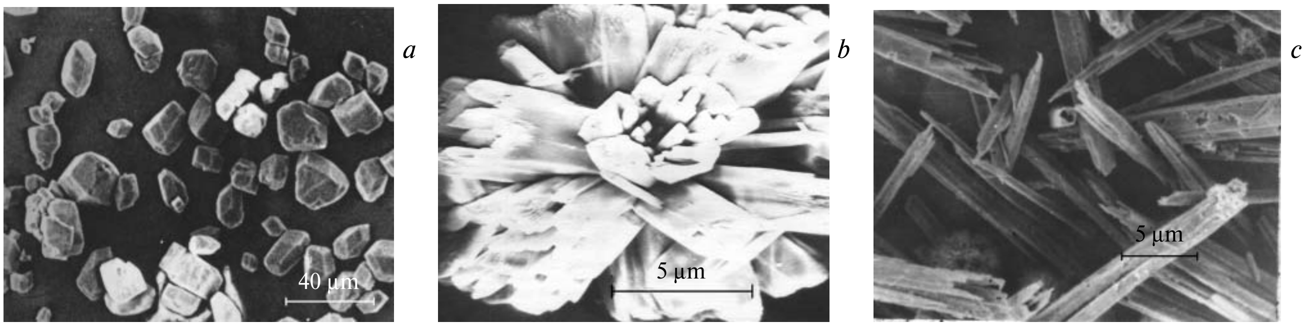

Fig. 7. Typical shapes of crystals of α- (*a*), α′- (*b*), and γ-AlH$_3$ (*c*).

up to 10 GPa and short heating to 800 °C. Thus, it can be concluded that all the three phases obtained in our and earlier[2] works are metastable relative to the α-AlH$_3$ phase, which is also metastable ($\Delta G = 11.11$ kcal mol^{-1}).[15] Since this conclusion agrees well with the known rule of Oswald′s steps, we can claim that, in the framework of the synthesis method considered, even when the solid phase contains no less dense aluminum hydride modifications (first of all γ-phase), this indicates a high rate of transition to the more stable α-phase rather than their absence.

When octane was used as the second component of the mixed solvent, mixtures of the γ- and α′-phases were obtained in the best case in a yield ≤20%. In the presence of other low-boiling alkanes, only the "dead" solvate AlH$_3$·0.31Et$_2$O crystallizes from the solution. This fact indicates a certain role of the π-system of the aromatic hydrocarbon in the mechanism of etherate desolvation and the crystal growth of the inorganic polymer.

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