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Role of hydrogen in stabilizing new hydride phases or altering old ones

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Abstract

The role of hydrogen impurities in many of the more active metals in the formation of ternary compounds has often not been considered or recognized when these reactants do not contain significant metal hydride phases. This is a particular problem because most phase identifications or structure determinations have traditionally depended on X-ray diffraction means. Extended investigations have established that the alkaline-earth metals, plus some other divalent metals, have evidently often contributed substantial amounts of hydrogen, and this feature has led to numerous erroneous reports of supposed binary phases that form with the main-group (p) elements. Methods of detection and some ready means to avoid these problems will be described. The particularly serious examples that occur among phases reported with β-Yb_5Sb_3, Mn_5Si_3, and Cr_5B_3-type binary structures for pnictogen (As–Bi) and tetrel (Si–Pb) elements are detailed for 32 examples. Fluoride has proven to be useful as a stand-in for hydride in a variety of these systems.

Keywords: Zintl phases; Hydrogen impurities; Interstitial atoms; Synthesis and structure; Fluoride vs. hydride

1. Introduction

Compounds formed between alkali, alkaline-earth, or rare-earth metals and the main group p-elements have been major players in the development of diverse structural and bonding aspects of solid state chemistry. The main-group components most often feature the triels (Ga family, *Tr*), tetrels (Si family, *Tt*), the pnictogens (P family, *Pn*), or the chalcogens. One common feature of many products in these systems is a predominance of closed shell compounds, the so-called Zintl phases [1], in which the electrons formally donated by the cations fill all valence shells of the anions, which may be simple or complex. We became involved in the question of phase stabilization by unrecognized impurities when faced by contradictions or inconsistencies among our results, or between ours and those in the literature, or by an inability to obtain a reported compound in high yield. Common impurity candidates are C, N and O, and our studies have led to the discovery of broad categories of stuffed metallic derivatives of the common hexagonal Mn_5Si_3-type structure [2]. We have since found that hydrogen can be a particularly pervasive and insidious problem among a variety of structure types. Our explorations have particularly focused on pseudo-binary 5–3 systems of the alkaline-earth metals (*Ae*: Ca,Sr,Ba). These historically appear to have been the most hydrogen-contaminated commercial materials, although other active metals or their reduced compounds can become contaminated through careless handling (Hydrogen is usually retained at least in part when the active metals react with smaller amounts of water). Systematic studies by common structure type among alkaline-earth metal phases have also been extended to include those with other divalent metals where they exist, viz. Sm, Eu, Yb.

(1) The first investigations stemmed from an inability to sort out the formation of hexagonal Mn_5Si_3-type from orthorhombic β-Yb_5Sb_3-type pnictides for many dipositive metals [3–5]. In fact, all eight examples assigned to the latter structure type were found to be valence hydrides $(A^{II})_5Pn_3H$ with what is now better termed the orthorhombic Ca_5Sb_3F structure type [3]. This was the first instance in which we utilized fluoride as a good stand-in for hydride as the former is easily located by modern X-ray diffraction means. (2) For numerous Mn_5Si_3-type reactants, the pnictide hydride forms first, or only, via occupation of a well characterized octahedral cavity therein [2,6]. (3) Similar events have shadowed the chemistry of the many A_5Tt_3 phases formed between divalent metals and the Tt (tetrel=Si–Pb) elements that supposedly occur in tetragonal Cr_5B_3-type structures. Here, hydride is

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readily incorporated into an existing but generally unrecognized tetrahedral cavity. These ternary examples fall into two categories: (a) Those containing tin or lead that are generally stable *only* as the stuffed Cr_5B_3 structure type and not as the binary phases reported in eleven publications [7]. (b) In nine more complicated instances, evidently *both* the binary and the ternary (hydride) silicides and germanides exist in a continuous heavy atom (Cr_5B_3) structure type [8]. Most of the 14 earlier reports appear to pertain to the latter. Preliminary extensions of these studies to the surprising, more electron-deficient triel (Ga, In, Tl) derivatives in the same structure type show that both true binaries and at least one unique hydride exist [9]. (4) Understandably, other unrecognized hydrides also exist, for example the Zintl phases $Ba_5Ga_6H_2$ [10] and $Ba_{21}M_2O_5H_{22+x}$ (M=Si, Ge, Ga, etc.) [11]. In general, all of the reported hydrogen-free compositions that we have studied are electron-rich, or potentially so, and we presume that the ability to accommodate H^- in small cavities defined by cations and the Madelung energy gain therefrom are in general much of the driving force for hydride formation.

2. Methodology

The reactions have generally been run in welded Ta containers, and glovebox manipulations and Guinier powder diffraction for phase identification have been utilized, the latter with Si as an internal standard in order to secure more precise lattice dimensions.

Alkaline-earth-metal–hydrogen systems show substantial α-phase solid solution areas below a two-phase region with AeH_2 [12]. In 1987, the hydrogen contents of the better commercial alkaline-earth metals were estimated to range between ~5 at% for Ca to ~20 at% in Ba [13]. Present samples are better, but not free of hydrogen. The hydrogen dissociation and metal vapor pressures above these systems are similar at practical sublimation or distillation temperatures, such that the condensed metals tend to reabsorb evolved hydrogen. However, careful procedures allow the hydrogen to be largely removed first in high vacuum at temperatures 100–200 °C below the respective melting points, before the metal transfer ensues.

In fact, there are more practical and direct ways to ensure the absence of hydrogen. Tantalum (or niobium) is clearly the container of choice for these systems, and this becomes appreciably permeable only to hydrogen at ~550 °C or above. In essence, any hydrogen in the otherwise pure reactants can be readily pumped out from the container at higher temperatures when this is maintained in a high vacuum ($\leq 10^{-5}$ Torr). Thus, a short while at ~1000 °C is quite effective, after which the contents can be equilibrated at lower temperatures selected according to expected phase relationships. A prior cleaning of the active (especially alkaline-earth) metals by this means is also suitable for subsequent multiple reactions [4,14].

Hydride or not? This is easily and effectively tested by running pairs of synthesis reactions in Ta—one under dynamic vacuum (dv hereafter) and one loaded with hydrogen (as AeH_2, etc.) and sealed within an evacuated and well-flamed fused SiO_2 container (sc). Use of the sealed silica jacket with a previously dehydrogenated metal component may not be as clean because some hydrogen (as H_2O) will be evolved from the silica, especially at 850–900 °C and above. Careful attention to lattice dimensions can readily identify situations in which nonstoichiometric solution regions exist. The presence of hydride inevitably contracts the cell, presumably by reducing the repulsion among the cations that surround a suitable cavity in the 'clean' system. Fluoride syntheses have generally been run under dv conditions to avoid any competition from hydrogen impurities. The more refractory AeF_2 reactants appear to require high temperatures in the initial stages [3,5].

Yields are an important and often neglected aspect of studies designed to correctly discern the compositions of phases. The phase rule does work, and an ability to synthesize a 'pure' phase (≥95–100%) by suitable adjustment of reactants and conditions is a valuable criterion as to whether the composition assignment is correct, particularly with respect to impurities. This has often been the important missing step with what have turned out to be hydrides. Practicabilities, e.g. incongruent melting problems, may force one to accept lower ~85–90% yields (judged on the basis of relative scattering powers for X-rays). Second phase detection limits are probably of the order of 3–5%.

3. Hydride results by structure type

3.1. β-Yb_5Sb_3-type [3–5]

This situation was particularly egregious as prior reports on, e.g. Ca_5Sb_3 and Sr_5Bi_3, were inconsistent as to whether the hexagonal Mn_5Si_3-type or the new orthorhombic β-Yb_5Sb_3 structure applied. None of the three reports on these compositions gave yields or evidence of both phases. As a clue to probable impurity levels, several of the earlier studies also noted the presence of Ae_2Pn phases that were later shown to actually be Ae_4Pn_2O compounds. At first, we inevitably found mixtures of both 5–3 structures, and no systematics seemed to interrelate them except that higher temperatures or excess Ae favored more of the β-Yb_5Sb_3 type, for good reasons. Fortuitously, fluoride was discovered to quantitatively yield the troublesome 'β-Yb_5Sb_3' type products as Ca_5Sb_3F and Ca_5Bi_3F [3], significant because fluoride will often substitute on a hydride site, and vice versa [15,16].

A comprehensive study of plausible $(A^{II})_5Pn_3$ systems established that all compounds reported to have β-Yb_5Sb_3

structures were in fact hydrides. Table 1, part 1 lists these, one new member (Sm_5Bi_3H), and four examples of analogous fluorides, all with the orthorhombic Ca_5Sb_3F structure (Fig. 1a) [4]. Fluoride analogues of interstitial hydrides have formed for all examples discussed in this article for which the reactions were attempted (except with $Mn_5Si_3H_x$-type products). To make the points clear, the characteristics of the reactions that yield Ca_5Sb_3, Ca_5Sb_3H or Ca_5Sb_3F in high yields are laid out in Scheme 1, emphasizing the contrasting results when hydrogen reactions are carried out under sealed container (sc) or dynamic vacuum (dv), respectively. Interconversions between the hydride extremes are completely reversible.

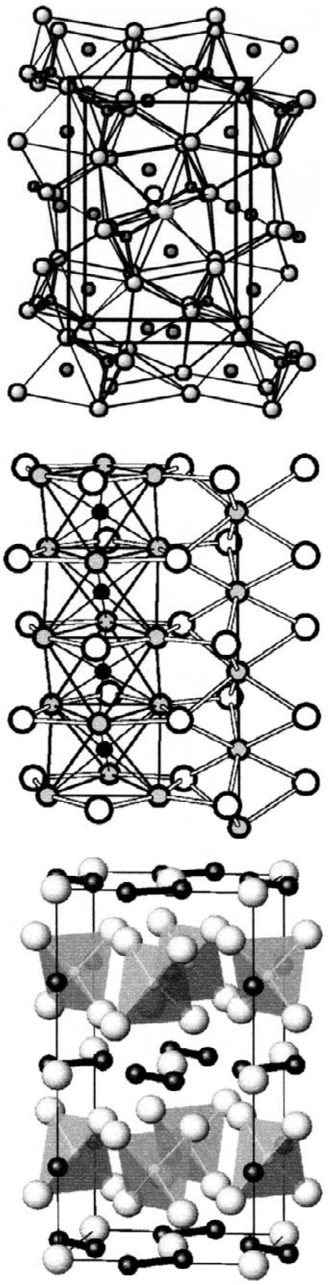

Fig. 1. (a) The orthorhombic Ca_5Sb_3F (vice-‘β-Yb_5Sb_3’) structure with Ca, Sb and F as larger open, medium shaded, and smaller black circles, respectively. Fluoride or hydride lies in the tetrahedral cavities, heavy bonds. Lighter lines interconnect Ca atoms only to illustrate the polyhedral construction. (b) The hexagonal Mn_5Si_3Z-type structure of $Ba_5Sb_3H_{-0.7}$. Larger open, medium shaded, and smaller black spheres represent Sb, Ba and partial H atoms, respectively, the last falling in trigonal antiprismatic cavities of Ca. (c) The tetragonal stuffed Cr_5B_3-type structure of Ca_5Ge_3F, with Ca, Ge and F atoms represented as larger open, medium black, and small white spheres, respectively. The last lie within the shaded Ca_4 tetrahedra.

Table 1
Stable $(A^{II})_5M_3X$ phases for M=As–Bi, Si–Pb, X=H, F

(1) Orthorhombic Ca_5Sb_3F type ($Pnma$) for Pn=Sb, Bi[a]	
Ca_5Pn_3H	Ca_5Pn_3F
Sr_5Pn_3H	Sr_5Pn_3F
Sm_5Bi_3H	–[b]
Eu_5Pn_3H	–
Yb_5Pn_3H	–
(2) Hexagonal $Mn_5Si_3H_x$ type ($P6_3mmc$) for pnictides, $x \leq 1$[c]	
$Ca_5As_3H_x$	–
$Sr_5As_3H_x$	–
$Eu_5As_3H_x$	–
$Yb_5As_3H_x$	–
$Sm_5Sb_3H_x$	–
$Ba_5Sb_3H_x$	–[d]
$Ba_5Bi_3H_x$	–
(3) Tetragonal Cr_5B_3X type ($I4/mcm$) for tetrels Si–Pb, X=H, F	
(a) No stable Cr_5B_3-type binary phase, Tt=Sn, Pb	
Ca_5Sn_3H	Ca_5Sn_3F
Ba_5Tt_3H	Ba_5Tt_3F
Eu_5Tt_3H	–[b]
$Yb_{53}SnH$	–
Sr_5Pb_3H	Sr_5Pb_3F
(b) Both Cr_5B_3-type binary and the ternary hydride exist, Tt=Si, Ge	
Ca_5Tt_3H	Ca_5Tt_3F
Sr_5Tt_3H	–[b]
Ba_5Tt_3H	Ba_5Si_3F
Eu_5Tt_3H	–
Sr_5Sn_3H	–

[a] All binaries listed are Mn_5Si_3 type and take up some H before transformation.

[b] Other fluoride syntheses were not attempted.

[c] All have Mn_5Si_3-type binaries. No fluorides and no transformation to other structures with H.

[d] No fluoride with this structure forms.

In all cases, the hydride interconversion apparently involves two nonstoichiometric phases, a partially filled hexagonal $Mn_5Si_3H_y$-type and the orthorhombic Ae_5PnH_x, both of which are probably substoichiometric at the conversion limit. A few results for the phase distribution in the $Ca_5Sb_3H_x$ system as a function of the loaded x are shown in Fig. 2. The difference in Mn_5Si_3-type yields seen between an sc reaction with clean Ca at $x=0$ (95%) and the dv reaction (~100%) (lower left) originate with the hydrogen impurity introduced by dehydration of the SiO_2

Binary: $$5\ Ca(H_x) + 3\ Sb \xrightarrow[\text{Ta, dynamic vacuum (dv)}]{800\ °C,\ 5\ hr} Ca_5Sb_3(s) + x/2\ H_2$$

hexagonal
Mn_5Si_3 type
$V = 996.1$ Å^3

Hydride: $$4.5\ Ca + 0.5\ CaH_2 + 3\ Sb \xrightarrow[\text{sealed Ta + SiO}_2\text{ containers (sc)}]{\text{Slow cool, 1100°– 650°C, 40 hr}} Ca_5Sb_3H(s)$$

orthorhombic
(Ca_5Sb_3F type)
$V = 991.3$ Å^3

Fluoride: $$4.5\ Ca + 0.5\ CaF_2 + 3\ Sb \xrightarrow[\text{Ta, dv}]{1250\ °C,\ 2\ hr;\ 850°C,\ 4\ hr} Ca_5Sb_3F(s)$$

orthorhombic
("β-Yb_5Sb_3")
$V = 1004.7$ Å^3

Scheme 1. Characteristics of the reactions that yield Ca_5Sb_3, Ca_5Sb_3H or Ca_5Sb_3F in high yields.

jacket (4 h, 1100 °C; slow cooling to 650 °C). The limiting values of y and x in a mixed phase composition, which define the breadths of the nonstoichiometry regions for the two phase, reflect the relative stabilities of the two hydride phases at equilibrium (Ranges of lattice constant variations within each also give qualitative measures). Small cations and large anions favor the Ca_5Sb_3F-type hydride with hydrogen in a tetrahedral cavity of cations relative to its being bound in an octahedral site in Mn_5Si_3–H_y products (below). Thus Ca_5Bi_3 is a very good getter for hydrogen, better than Y metal, such that quenching a dv run from 1100 °C was necessary to get a 95% yield of hexagonal $Mn_5Si_3(H)$ type, whereas only 5% of this occurred after an equilibration for 14 days at 850 °C under 'high' vacuum. Second best in this respect is Yb_5Bi_3H. The upper limits are thought to be near $x=1$, and this was quantified for $Ca_5Bi_3D_{0.93(3)}$ by neutron powder diffraction.

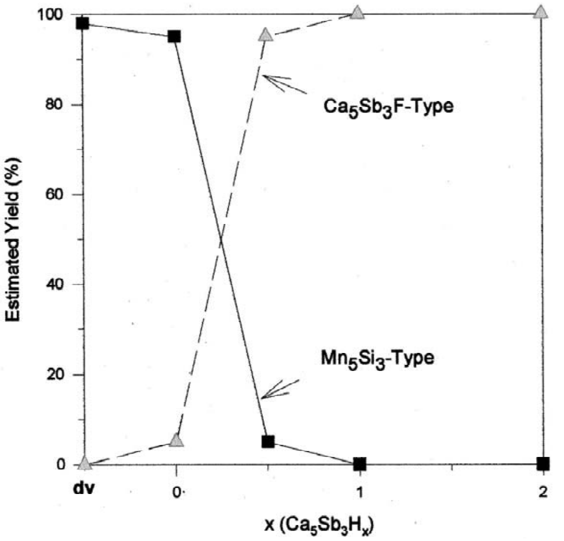

Fig. 2. The proportions of $Ca_5Sb_3H_n$ phases formed with the Mn_5Si_3-type structure (solid squares) vs. the Ca_5Sb_3F-type structure (shaded triangles) as a function of x loaded in $Ca_5Sb_3H_x$ reactions in sealed containers.

3.2. $Mn_5Si_3H_x$-type [6]

Hydrogen-poor or -free limits for all the Ca_5Sb_3F-type pnictide hydrides in Table 1 part 1, consist of hexagonal Mn_5Si_3-type phases, and these take up some amount of hydrogen in the octahedral site—the solid black circle in Fig. 1b—before they transform to the orthorhombic hydrides. Lattice constant shifts make this clear, but none has been quantified. Other related binaries that do not form the competitive orthorhombic hydride generally absorb more hydrogen in a hexagonal $Mn_5Si_3H_x$-type structure, and these are listed in Table 1 part 2. The group includes many of the arsenides. Upper x limits for these $(A^{II})_5PnH_x$ limits have not been determined, but lattice constant changes suggest x is particularly substantial for Ca–As, Yb–As, Ba–Sb and Ba–Bi. The one fluoride synthesis attempted with Ba_5Sb_3 did not form; this and related hosts are known to bind the larger chloride and bromide [3] but the small hard fluoride is an unlikely interstitial. Presumably it was substantial amounts of hydride impurities, or a lack of care in looking, that obscured the earlier discovery of 13 (out of the possible 15) stable $Ca_{16}Pn_{11}$-type phases for all five A^{II} [17].

3.3. *Cr_5B_3-type hydrides*

This group of 5–3 compounds structurally contain equal numbers of monomers and dimers of the tetrel main-group elements (Tt=Si, Ge, Sn, Pb). The group is too electron-poor to form any Mn_5Si_3-type phases with only isolated main-group elements. Two types of hydride relationships involve the characteristic tetragonal structure.

3.3.1. *No stable binary examples [7]*

This group of seven compounds (Table 1 part 3a) illustrate how serious the hydrogen impurity problem may be. None of the ten earlier reports of these as binary phases is correct, all binaries actually being other structure types (e.g. W_5Si_3) or mixtures of other compositions. The hydrogen contents seem substantial (x~1), but only $Ca_5Sn_3D_{1.04(2)}$ was quantified by neutron powder diffraction. In no case did the loading of excess hydrogen (beyond that for the monohydride) into any of the 5–3 systems described in this article result in further changes in lattice dimensions or the appearance of a new phase that would indicate that there is a means to bind more hydrogen.

All the systems tested yielded the same structure type. The structure of two each of these as the fluoride and as pseudo-binary hydrides were verified by single crystal X-ray means. A ~[100] view of the tetragonal structure of Ca_5Sn_3(H,F) is shown in Fig. 1c. The intermediate-sized black spheres are Sn, as dimers at $z=0$, 1/2 and monomers around $z=1/4$, 3/4. The shaded tetrahedra around the latter planes are composed of Ca2 atoms that encapsulate H or F. This scarcely recognized cavity is also occupied in the isotypic La_5Pb_3(O,N) [20], but this electron-richer structure contains only lead monomers.

It is noteworthy that the erroneous structures reported for some of these exhibit evidence of the unseen hydride in the shorter A2–A2 distances around the tetrahedral site. Thus, extended Hückel calculations with the supposed binary structure dimensions show a substantial half-filled band originating from A2 atoms around E_F, unused nonbonding states that are converted to a bonding band when H is added. The same applies to 'β-Yb_5Sb_3' reports.

Evidently the relatively consistent formation of substantial amounts of hydrides in earlier studies of some systems was sufficient that it also concealed the existence of, among others, the novel binary phases $Ae_{31}Tt_{20}$. These occur at 60.8 at% Tt for $Ca_{31}Sn_{20}$, $Sr_{31}Pb_{20}$ and $Yb_{31}Pb_{20}$ vs. 62.5 at% for Ae_5Tt_3 [18]. This circumstance also applies to the related $Yb_{36}Sn_{23}$ at 61.0 at% Yb [19]. The earlier studies usually didn't indicate whether any other phases were also present along with the 'A_5Tt_3' product.

3.3.2. *Both binary and ternary examples*

The group for which pure A_5Tt_3 and A_5Tt_3H phases are both stable (Table 1 part 3b) [8] emphasizes a generic effect of main-group element size. With one exception (SrBSn), the present group includes just Tt=Si or Ge members whereas the former (stuffed-only) examples occur solely for Tt=Sn or Pb. In the present case, the competitive binary phases must be more stable with smaller Tt. A reticulated model of the structure that reflects the relative sizes of the metal atoms suggests a reason. The dimers are bound in augmented rhomboidal prisms with the bond axes along the long prism dimension. This would appear to be too tight to contain the larger Sn and Pb dimers in the unknown binary examples. On the other hand, contraction of the tetrahedra on hydrogen (hydride) binding acts in a concerted way through shared edges and polyhedra to lengthen these dimer cavities, preferentially stabilizing the larger dimers only in the presence of hydrogen.

3.4. *Others*

We have explored some of the triel (Tr=Ga, In, Tl) systems that reportedly form Cr_5B_3-type structures with the same cations and have established that several are true binaries, even though these are quite electron deficient with respect to formation of the ideal (improbable?) valence anions Tr^{5-} and Tr_2^{8-}. But at least one report actually concerned a hydride, Sr_5Tl_3H [9]. We are also aware that at least two reported $(A^{II})_5Tt_4$ compounds appear to be hydrides.

Errors in two other reported 'intermetallic' structure types were established following considerations of the reported stoichiometries, whether these might be Zintl (valence) hydrides, and some malaprop displacement ellipsoids, namely $Ba_5Ga_6H_2$ [10] and $Ba_{21}M_2O_5H_{22}$, M=Si, Ge, etc. [11]. The germanium phase is a diamagnetic semiconductor, as its constitution would suggest. Numerous other such errors presumably exist in the literature.

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