1892 *Inorg. Chem.* **1998,** *37,* 1892−1899

$Ba_{21}Ge_2O_5H_{24}$ and Related Phases. A Corrected Structure Type and Composition for a Zintl Phase Stabilized by Hydrogen

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Received October 22, 1997

Syntheses of the so-called "suboxide" phases $Ba_{21}T_2O_5$ (T = Ge, Si, Ga, In, Tl) are achieved only in the presence of hydrogen. The heavy-atom structure of $Ba_{21}Ge_2O_5H_{24}$ at room temperature was redetermined by single-crystal X-ray diffraction and found to be primitive trigonal symmetry ($P3_121$ (No. 152), $Z = 6$, $a = 14.4227(5)$ Å, $c = 35.332(3)$ Å) instead of the previously refined cubic ($Fd\bar{3}m$) result. The change greatly improves the heavy-atom parameters. Twenty-four independent deuterium atoms have also been located by time-of-flight neutron diffraction. The structure contains Ba^{2+} cations, and three different types of monatomic anions, corresponding to the oxidation states $(Ba^{+2})_{21}(Ge^{-4})_2(O^{-2})_5(H^-)_{24}$. The deuterium atoms occupy tetrahedral, square-pyramidal, and octahedral barium interstices while the oxide anions lie in nearly regular octahedral barium polyhedra. The germanide anions are surrounded by 12 barium atoms in a distorted icosahedral configuration. Property measurements show that $Ba_{21}Ge_2O_5H_{24}$ is diamagnetic and is a semiconductor (or insulator). The analogues $Ba_{21}Tr_2O_5H_x$, Tr = Ga, In, Tl, are isotypic with the heavy-atom structure of the title phase and presumably contain 22 hydride ions.

Introduction

The formation, stoichiometry, and structure of barium-rich compounds formed by the triel (Tr) (group 13) and tetrel (Tt) (14) main-group elements have been controversial and incomplete. In 1966, Bruzzone first studied the three binary Ba−Tr (Tr = Ga, In, Tl) phase diagrams and found a new family of the interesting phases that he believed to be $Ba_{10-12}Ga$, $Ba_{13}In$, and $Ba_{13}Tl$, respectively.[2] The first structure in this family was determined by film methods in 1979 by Fornasini and Merlo[3] to be cubic $Ba_{10}Ga$ ($Fd\bar{3}m$), which they believed to be isotypic with $Al_{10}V$. In 1995, five $Ba_{21}M_2O_5$ compounds (M = Ge, Si,[4] Zn, In, Tl[5]) were reported by Röhr to have a cubic structure quite similar to that of $Ba_{10}Ga$. However, one cation type in the refined structures of the first two members showed quite large ellipsoids. This group of compounds is intriguing since the so-called "suboxides" appear to have extraordinarily high electron excesses.

On the other hand, correctly characterized compounds formed between active alkaline-earth metals (Ae) and main-group elements often conform to simple Zintl−Klemm valence rules in which the latter elements achieve octet valence states.[6] Therefore, it was considered possible that these "unusual" compounds might be stabilized by additional impurities. Oxygen contamination in Zintl phases is relatively easily recognized because of its relatively high X-ray scattering power. On the other hand, hydrogen components in many alkaline-earth metal phases have been relatively ignored because contamination of the metal by hydrogen has often gone unrecognized,[7] largely because it is generally not "seen" by X-ray diffraction. Recently, we reported on a series of Zintl phases of the alkaline-earth metals that are stabilized by hydrogen: $Ba_5Ga_6H_2$,[8] Ae_3TtH_2 (Ae = Ca, Yb; Tt = Sn, Pb),[9] Ae_5Pn_3H (Pn = As, Sb, Bi) ("Yb_5Sb_3"-type),[7,10] and Ae_5Tt_3H (Tt = Si, Ge, Sn, Pb) and Sr_5Tl_3H (stuffed Cr_5B_3 or La_5Pb_3O-type[11]).[12] Here we present both the syntheses of the five compounds $Ba_{21}Tt_2O_5H_{24}$ (Tt = Ge, Si) and $Ba_{21}Tr_2O_5H_x$ (Tr = Ga, In, Tl, $x \sim 22$), in which hydrogen is an essential component, and the corrected structure of $Ba_{21}Ge_2O_5H_{24}$ as determined by X-ray single-crystal and neutron powder diffraction means.

Experimental Section

Syntheses. Sublimed barium (Aldrich-APL, 99.9%) and calcium (APL Engineered Materials, 99.99%), their hydrides, and the products of the present studies are very sensitive to air and moisture, and they were therefore handled only in He- or N_2-filled gloveboxes ($H_2O < 1$ ppm vol). Binary barium and calcium hydrides were prepared from the respective metals by reaction with hydrogen (600 Torr, Matheson, 99.999%) at 800 °C for 12 h. Their Guinier X-ray powder patterns showed only the binary hydrides were present. Barium oxide was prepared by decomposition of barium carbonate (Baker, 99.8%) for 24 h in an open Ta container under a dynamic vacuum ($\leq 10^{-5}$ Torr) at 1000 °C. Its Guinier X-ray pattern showed only the presence of BaO. The other elements used were Aesar Ge (5-9's), electronic grade Si, Johnson-Matthey Ga and Tl, and Cerac In (5-9's). All other syntheses reported in this article were carried out in welded Ta containers.

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$Ba_{21}Ge_2O_5H_{24}$. At the beginning, this compound was obtained from reactions of BaH_2, BaO, and Ge in a sealed system at 1100 °C for 4 h followed by slow cooling at 20 °C h^{-1}. Excess Ge was needed for an otherwise high-yield synthesis, perhaps because the ground Ge particles did not completely react with BaH_2 and BaO. It was later found that prereaction of Ge with Ba and BaO solves this problem. The Ba, BaO, and Ge in an overall proportion $Ba_{21}Ge_2O_5$ (total amount: 250−500 mg) were welded in a Ta container under Ar that was in turn placed in fused-silica tubing and connected to a high-vacuum source ($\leq 10^{-5}$ Torr). The assembly was heated at 1100 °C for 4 h to remove impurity hydrogen and to allow Ge to react completely with Ba metal and BaO to form Ba_3GeO,[13] and it was then cooled at 40 °C h^{-1} to 600 °C. The container was then charged with hydrogen to 600−700 Torr, held there for 1 h (presumably to form BaH_2), then heated to 1100 °C, and held there for 8 h (under H_2) followed by cooling at 20 °C h^{-1}. A parallel reaction under high vacuum and without H_2 gave a mixture of Ba_3GeO, BaO, and Ba. The final quaternary product had a shiny black color, was extremely sensitive to air, and gave a powder pattern that appeared to be single phase and to be in complete agreement with that calculated for the refined structure.

$Ba_{21}Ge_2O_5D_{24}$. The deuteride was prepared in the same manner but with D_2 instead of H_2 and double reactions. Three Ta containers were each loaded with 4.0 g of the appropriate mixture and treated as above. However, the deuteride product sought contained a small amount of unreacted materials. Therefore, the samples were transferred to new Ta containers which were welded and sealed again in fused silica, and the assembly was preheated to 300 °C under high vacuum to dehydrate the silica jacket somewhat. The systems were then charged with deuterium to 600−700 Torr, heated to 1100 °C, held there for 8 h, and cooled to room temperature at a rate of 40 °C h^{-1}. The main product was $Ba_{21}Ge_2O_5D_{24}$ (>90%), but BaD_2 (Co_2Si-type) (<5%) and Ba_3GeO (<5%) were also observed. Evolved water is possibly responsible for the oxide impurity because of the lack of a thorough baking of the SiO_2 in the second step. An 8.5 g mixture of the three samples was sealed under He into a gasketed vanadium cylinder with an inner diameter of 10 mm for the neutron diffraction experiment.

A Ta container was loaded with ∼1 g of this $Ba_{21}Ge_2O_5D_{24}$ product, welded under Ar, and then heated to 1100 °C under high vacuum for 4 h followed by cooling to room temperature. The X-ray pattern of the product showed only Ba_3GeO, BaO, and Ba.

$Ba_{21}T_2O_5H_x$ (T = Si, Ga, In, Tl). Two Ta containers were used in the preparation of each compound. The first was loaded with Ba metal, BaO, and T (total ∼250 mg) at the composition $Ba_{21}T_2O_5$. The second Ta tube was charged with CaH_2 (∼40 mg) and Sn (∼120 mg). The two containers were each welded under Ar and sealed together in a carefully flamed silica jacket under high vacuum. The double containers were slowly heated to 1100 °C at the rate of 40 °C h^{-1}, kept there for 4 h, and slowly cooled to room temperature. The reaction process may perhaps be as follows: Ba reacts with Si, Ga, In, or Tl and BaO in the first container at a low to intermediate temperature, the CaH_2−Sn reaction produces H_2 (plus CaSn) in the second at an intermediate temperature, and the H_2 diffuses into the other Ta container (>500 °C) to form the quaternary hydride. The amounts of CaH_2 loaded were to give compositions $Ba_{21}Si_2O_5H_{24}$ and $Ba_{21}Tr_2O_5H_{22}$, respectively. The final products had shiny black colors and were extremely sensitive to air. Their Guinier patterns were very similar to that of $Ba_{21}Ge_2O_5H_{24}$ and showed the yields to be about 90%. Heating the Ga, In, and Tl hydride products under a high vacuum at 1100 °C gave mixtures of BaO, Ba, and unknown phases.

Structural Studies. Guinier patterns were obtained from ground samples to which NIST silicon ($a = 5.43088$ Å) had been added as an internal standard. These were mounted between pieces of cellophane tape and measured with the aid of an Enraf-Nonius Guinier camera, Cu Kα radiation ($\lambda = 1.540\ 56$ Å). The Guinier films were measured with a computer-controlled microdensitometer,[14] and data were analyzed by the program SCANPI[15] to obtain the peak positions. Patterns of the germanium compound were indexed on the basis of both the cubic and trigonal single-crystal structure solutions, and the lattice parameters were refined for each by least-squares methods from 16 to 20 indexed 2θ data. The structures of other $Ba_{21}T_2O_5H_x$ phases (above) were so established by powder data to be isotypic with the cubic pseudocell of the Ge compound, which generally cannot be distinguished from the correct trigonal structure by Guinier means. Cubic and trigonal lattice parameters similarly refined from the same Guinier film data are summarized in Table 1 for the loaded compositions along with literature data for the evidently equivalent ternary compositions. In no case did the trigonal lattice constants deviate significantly from the cubic equivalents, $c/a = 6^{1/2}$.

Table 1. Lattice Dimensions (Å, Å^3) of Isotypic $Ba_{21}T_2O_5H_{22-24}$ Phases, T = Ge, Si, Ga, In, Tl

compd	cubic cell[a] ($Fd\bar{3}m$, Z = 8)	trigonal cell[b] ($P3_121$, $Z = 6$)
$Ba_{21}Ge_2O_5H_{24}$	$a = 20.3971(5)$ $V = 8486.0(6)$	$a = 14.4227(5)$, $c = 35.332(3)$ $V = 6364.6(5)$
"$Ba_{21}Ge_2O_5$"[c]	$a = 20.398(9)$ $V = 8487(7)$	
$Ba_{21}Ge_2O_5D_{24}$	$a = 20.388(1)$ $V = 8474(1)$	$a = 14.415(1)$, $c = 35.322(6)$ $V = 6356(1)$
$Ba_{21}Si_2O_5H_{24}$	$a = 20.3951(8)$ $V = 8483.7(9)$	$a = 14.4207(8)$, $c = 35.331(4)$ $V = 6363.0(7)$
"$Ba_{21}Si_2O_5$"[c]	$a = 20.383(10)$ $V = 8469(7)$	
$Ba_{21}Ga_2O_5H_{22}$	$a = 20.4659(9)$ $V = 8572(1)$	$a = 14.4704(8)$, $c = 35.456(5)$ $V = 6429.6(8)$
"$Ba_{10}Ga$"[d]	$a = 20.52(1)$ $V = 8640(8)$	
$Ba_{21}In_2O_5H_{22}$	$a = 20.715(1)$ $V = 8888(2)$	$a = 14.649(1)$, $c = 35.870(8)$ $V = 6665(1)$
"$Ba_{21}In_2O_5$"[e]	$a = 20.760$ $V = 8947$	
$Ba_{21}Tl_2O_5H_{22}$	$a = 20.6510(8)$ $V = 8807(1)$	$a = 14.6026(9)$, $c = 35.767(5)$ $V = 6605.0(9)$
"$Ba_{21}Tl_2O_5$"[e]	$a = 20.681$ $V = 8845$	

[a] Guinier data for present results ($\lambda = 1.540\ 562$ Å, 22 °C). [b] The equivalent trigonal cell data refined from the same Guinier pattern. The tuned trigonal data for $Ba_{21}Ge_2O_5H_{24}$ and $Ba_{21}Ga_2O_5H_x$ on the diffractometer differed by $\leq 3\sigma$. [c] Reference 4. [d] Reference 3. [e] Reference 5.

X-ray Single-Crystal Diffraction. Crystals of the germanium phase were sealed in thin-walled capillaries and checked for singularity by Laue photographs. Room-temperature data were collected from one on a Rigaku AFC6R rotating-anode diffractometer (Mo Kα radiation, graphite monochromator). Twenty-five centered reflections located and centered by a random search starting at $2\theta \sim 12°$ were used for a preliminary assessment of the symmetry. One relatively strong reflection in this orientation set indicated a primitive trigonal unit cell, a symmetry that was also confirmed by subsequent precession photographs (*hk*0 to *hk*2) taken with Ni-filtered Cu Kα radiation. All other diffractometer reflections were deleted, and 49 new ones were located starting at $2\theta \sim 20°$ in order to obtain a better orientation matrix. Diffraction data were measured in an $\omega-2\theta$ scan mode for $2\theta < 55°$. Intensities of three standard reflections measured every 150 reflections during the data collection did not change significantly. Analyses of the intensity characteristics indicated a $\bar{3}m1$ Laue symmetry and a variety of trigonal space groups. The trigonal setting is responsible for about 10% of the total observed reflections (at $3\sigma_I$).

The trigonal structure was solved by direct methods via SHELXS.[16] The atomic positions and thermal parameters were refined with the TEXSAN[17] package on a VAX station. Assignment of the space group was made through comparisons of the results obtained in various primitive trigonal space groups. Those with a centering or mirror operation were excluded without complications by the direct methods

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Table 2. Selected Single-Crystal X-ray Data Collection and Refinement Parameters for $Ba_{21}Ge_2O_5H_{24}$[a]

fw	3133.30	μ, cm^{-1} (Mo Ka)	204.84
space group; *Z*	$P3_121$; 6	$R(F_o^2)$, R_w[b] for $I > 3\sigma_I$, %	8.5, 11.7
temp, °C	22	$R(F_o)$, R_w[c] for $I > 3\sigma_I$, %	7.4, 6.4
d_{calc}, g/cm^3	4.894		

[a] Lattice dimensions in Table 1. [b] $R = \Sigma||F_o|^2 - |F_c|^2|/\Sigma|F_o|^2$; $R_w = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w = \sigma_F^{-2}$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$; $w = \sigma_F^{-2}$.

results and by preliminary refinements which gave unusually large thermal parameters for Ba and high residuals. The remaining space groups were *P*321 (No. 150), $P3_121$ (No. 152), and $P3_221$ (No. 154). The space group $P3_121$ for the crystal selected was proven by the successful refinements. Absorption corrections were found to be crucial for this system because both Ba and Ge are strong absorbers of Mo Kα radiation ($\mu = 204.8$ cm^{-1}). The corrections were carried out according to ψ-scan curves for 10 strong reflections at different θ values and, after isotropic convergence, by DIFABS which gave lower *R*'s and smaller *U*'s.[18] The trigonal structure, including 24 hydrogen atoms with fixed positions obtained from subsequent neutron diffraction studies, was refined on F_o^2 by full-matrix least-squares methods with 3716 reflections with $F_o^2 > 1.0\sigma(F_o^2)$ and 108 variables. The relatively high residuals ($R(F_o^2) = 11.7$, $R_w = 12.6$) resulted from the fact that about 45% of the observed data fell in the region $1.0\sigma < F_o^2 < 3.0\sigma$. Thermal motion was restricted to isotropic since we felt that there were not enough strong primitive reflections for anisotropic refinement. The conventional residual factors (%) for those with $F_o^2 > 3\sigma(F_o^2)$ are $R(F^2) = 8.2$, $R_w = 11.0\%$ and $R(F) = 7.2$, $R_w = 6.3\%$. Some X-ray single-crystal data collection and refinement parameters are listed in Table 2. More details are given in the Supporting Information which, together with F_o/F_c tables etc., are also available from J.D.C.

Neutron Powder Diffraction. The atomic parameters and displacement amplitudes of hydrogen and oxygen were established with the aid of neutron powder diffraction data collected at room temperature overnight on the Special Environment Powder Diffractometer (SEPD) at the Intense Pulsed Neutron Source (IPNS) facility at Argonne National Laboratory. The SEPD is a time-of-flight powder diffractometer with multidetector arrays at fixed scattering angles. For this structural refinement, the high-resolution data from the $2\theta = 144.8°$ backscattering detector bank were used. The powder data were refined by the Rietveld method[19] with the PC version of the General Structure Analysis System (GSAS) by Larson and Von Dreele.[20] The final refinement included data in the range 0.60 Å < *d* < 4.0 Å (5103 profile points, 11 476 reflections).

At the beginning, attempts were made to locate deuterium positions in the face-centered-cubic cell (i.e., Röhr's model). Two D positions were found: D1 (96*g*) atoms in square-pyramidal barium polyhedra and D2 (96*g*) filling tetrahedral cavities. However, the Ba3 and D2 atoms had unusually large displacement amplitudes, i.e., $U_{iso}= 0.12$ Å^2 for Ba3 and 0.25 Å^2 for D2. Subsequently, we focused on a solution of the primitive trigonal structure to resolve the thermal parameter troubles. Since the Ba and Ge framework in $Ba_{21}Ge_2O_5$ was well established from the single-crystal X-ray study, D positions were located by successively placing a trial atom in an empty barium polyhedron, optimizing the Ba−D distances by the program ATOM 4.0, and then allowing either the temperature factor or the occupancy for each atom to refine. (Several still-larger cavities near Ba21 and Ba22 were also tested, but these all gave large ellipsoids (>0.4 Å^2) or near-zero or negative occupancies.) Twenty-four 6-fold D sites were so found: D1−D12 atoms (D1 in the cubic model), occupying the relatively larger square-pyramidal or octahedral holes formed by Ba, and D13-D24 atoms (D2 in the cubic model), filling the barium tetrahedra. Note that these are direct descendants of all 2 × 96 cubic sites since the primitive trigonal cell is 75% as large.

Table 3. Powder Neutron Data Collection and Refinement Parameters for $Ba_{21}Ge_2O_5H_{24}$

temp, °C	23	scattering lengths (10^{-12} cm)[b]	
no. of data	5103	Ba	0.525
no. of reflns	11 476	Ge	0.819
residuals,[a] %: R_p; R_{wp}	4.66; 6.95	O	0.581
χ^2	4.74	D	0.6674

[a] $R_p = (\Sigma|I_o - I_c|)/\Sigma I_o$; $R_{wp} = [\Sigma w(I_o - I_c)^2/\Sigma w I_o^2]^{1/2}$. [b] Reference 20.

In subsequent refinements, the Ba and Ge positions in the title phase were held fixed at the more accurate values from the single-crystal X-ray study. The groups of Ba, Ge, and O atoms were each constrained to have a fixed isotropic parameter, and likewise, for the two distinct groups of deuterium, D1−D12 and D13−D24, and these refined well. Two impurity phases, BaD_2 and Ba_3GeO, were also observed, and their proportions, lattice parameters, and positional parameters were included in the refinement; their relative amounts were found to be 4.4(3) and 5.1(2)% (by weight), respectively. The background function was a cosine Fourier series with 12 coefficients. Refinements of the phase fractions, background coefficients, and lattice and atomic parameters for the three phases diverged. Therefore, we separately refined the variables in two parts. The first included D and O positions, their collective thermal parameters, and the lattice parameters of the main phase, and the second, the remaining variables. These were cycled several times and essentially converged. The variables in the final cycle were positions of five oxygen and 24 deuterium atoms, five group thermal parameters, and two cell dimensions. The final conventional agreement indices were $R_p = 4.66\%$ and $R_{wp} = 6.95\%$ with a reduced χ^2 of 4.74. Some neutron data collection and refinement parameters are listed in Table 3.

The neutron diffraction pattern in Figure 1 shows the raw intensity data and, from top to bottom, the background, the individual contributions from the refined $Ba_{21}Ge_2O_5D_{24}$ and the impurities BaD_2 and Ba_3GeO with tick marks for the reflections included, and the difference between calculated and observed intensity profiles.

Physical Property Measurements. The electrical resistivity of $Ba_{21}Ge_2O_5H_{24}$ was measured by the electrodeless high-frequency "Q" method.[21] A fractionated ground sample with an average particle diameter around 340 μm was isolated and mixed with chromatographic Al_2O_3 in order to reduce contact between the sample particles. The mixture was loaded into a glass ampule and sealed under a vacuum. The Q measurements were made at 35 MHz over 100−295 K with readings every 15°. The magnetic susceptibility data were measured at 3 T over the range 6−300 K on a Quantum Design MPMS SQUID magnetometer. A special fused-silica container was used such that a 50-mg sample was held between the faces of two fixed silica rods. The assembly was evacuated, backfilled with He, and sealed. Data were corrected for container and core diamagnetism.

Results and Discussion

Syntheses. The compound $Ba_{21}Ge_2O_5H_{24}$ and its deuteride are synthesized in high yields by 1100 °C reactions of Ba, BaO, and Ge with H_2 (D_2) under a pressure of 600−700 Torr followed by slow cooling under the same gas pressure. Substantially all of the H_2 uptake occurs at the higher temperatures. The same reaction run at 1100 °C but under high vacuum gives only Ba metal, BaO, and the new Ba_3GeO.[13] The analogous compounds of Si, Ga, In, and Tl are again obtained only in the presence of hydrogen; reactions in a vacuum produce only BaO, Ba, and unidentified phases.

Alkaline-earth metals contaminated with oxygen are easily recognized because their white oxides usually appear only on the surface of metals and can be readily detected by X-ray diffraction. Of course, the monoxides can be removed by

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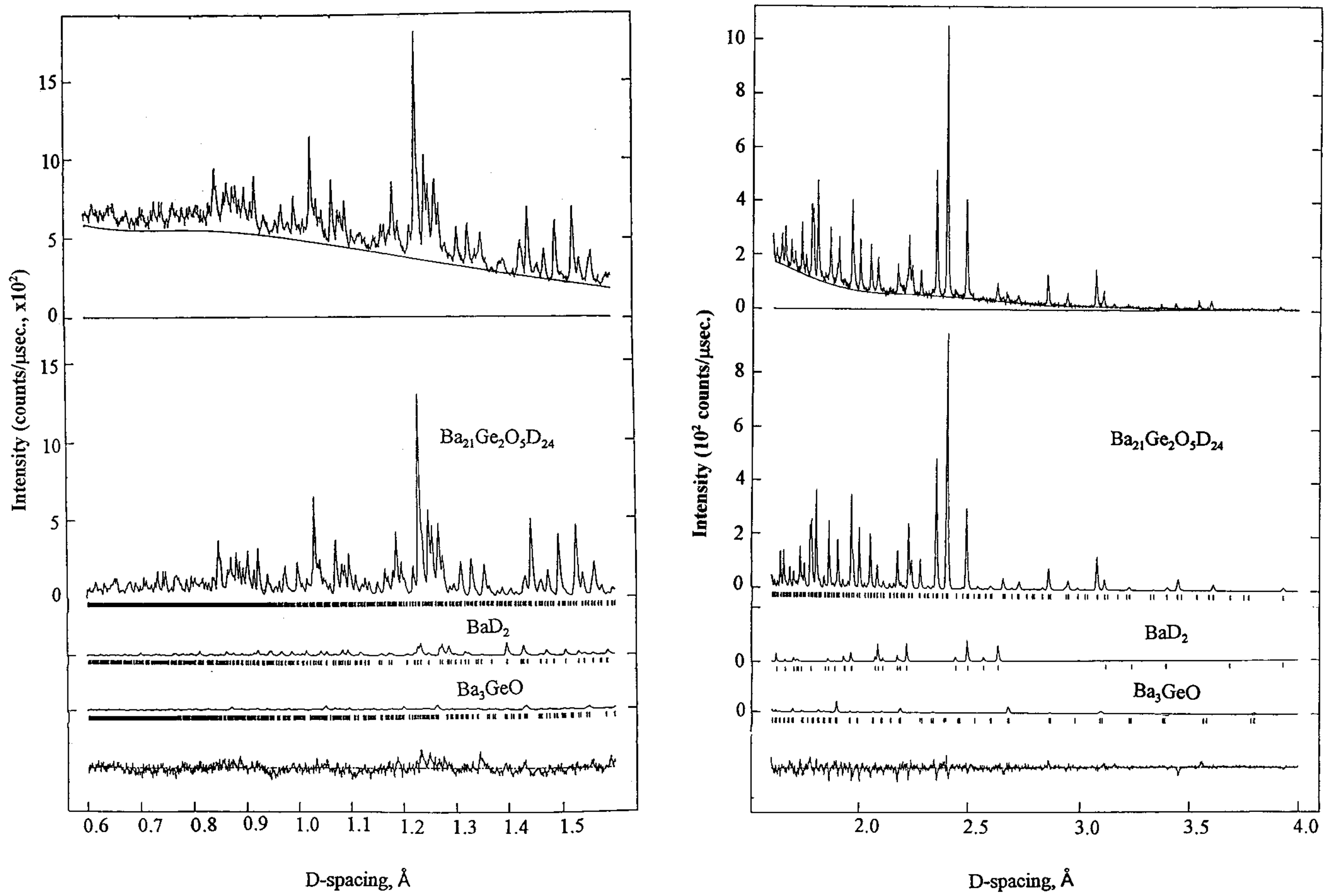

Figure 1. Neutron powder pattern of $Ba_{21}Ge_2O_5D_{24}$ divided into two regions, $d = 0.6-1.6$ and $1.6-4.0$ Å. From top to bottom: the experimental pattern with fitted background; the calculated patterns for the major and impurity BaD_2 and Ba_3GeO phases and the locations of the reflections used (tick marks); the difference spectrum on the same scale.

distillation without complications because of their relatively high melting points and very low volatilities or decomposition. However, the possibility of hydrogen contamination has been relatively ignored. The problem arises largely because of the ready diffusion of hydrogen (from metal−water reactions) into the metal in the solid solution (α) region where it is not directly discerned by X-ray techniques (except via small lattice constant changes). (In addition, good powder pattern data of these metals may be difficult to obtain by some methods even when hydride has precipitated.) The commercially available distilled alkaline-earth metals were at one time estimated to contain at least 5−20 atom % H for Ca−Ba, respectively,[22] and our experiences support these qualitatively, barium being the worst.[7,10,12] Further, the hydrogen in these metals is not easily removed by the usual distillation as the evolved H_2 is readily reabsorbed by the condensate. The permeability of Ta to hydrogen above about 500 °C is a useful property to accomplish the purification although, alternatively, the hydrogen can also be removed in high vacuum just below the temperature at which sublimation starts.[10]

Structural Description. The structure of $Ba_{21}Ge_2O_5H(D)_{24}$ was refined from both X-ray single-crystal and neutron powder diffraction data collected at room temperature. The final atomic coordinates, the isotropic-equivalent temperature factors, and their estimated standard deviations for the 22 Ba, 3 Ge, 5 O, and 24 D atoms in the independent unit are listed in Table 4. Important distances are given in Table 5, except that those within the Ba polyhedron about each D are contained in the Supporting Information. The compound is, to our knowledge, the first example of a Zintl phase stabilized by two types of nominal impurity anions. It also represents a novel structure.

The structure has a surprising complexity. It can be grossly described, to begin with, as a composite of two spherical-like components A and B, each of which is shown in Figure 2. The only proper symmetries are 2-fold axes normal to *c* and parallel to *a* or *b*, and only two Ge and two Ba atoms lie on these. In the A unit, a centering O4 atom (the cubic O2) is surrounded by six Ba atoms (the cubic Ba2) in an octahedral configuration. This Ba_6O unit is tetrahedrally fused twice through shared faces, once to four more O1,2,3,5-centered Ba octahedra and once to four Ge-centered Ba icosahedra. These eight O and Ge atoms form a strongly deformed cube, the larger Ge atoms lying further from the cube center and the starting O4 atom. Each of the four Ba octahedra in the outer tetrahedron is twice trigonally capped by three Ge and by three D atoms (D1−D12), the last face in each being capped by D atoms that lie in tetrahedral interstices in unit B (below). The distorted icosahedral polyhedron of Ba that surrounds each Ge is connected to three outer Ba_6O octahedra by face-sharing. Unit A has approximately T_d symmetry.

In the less regular unit B (Figure 2B), the centering Ba13 (cubic Ba4) is surrounded by 12 D atoms in an irregular configuration. This deuterium polyhedron is in turn surrounded by 16 barium atoms in the form of an approximate tetracapped truncated tetrahedron (Frank−Kasper 16). The entire barium polyhedron in B, unshielded by deuterium atoms, is illustrated in Figure 3 with the Ba5 (×2), Ba21, and Ba22 atoms that cap

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Table 4. Atomic Coordinates and Isotropic Thermal Parameters (×100 Å^2) for $Ba_{21}Ge_2O_5D_{24}$

atom[a]	Wykoff site	*x*	*y*	*z*	U_{iso}[b]	U_{iso}[c]
Ba1	6*c*	0.0045(9)	0.3904(8)	0.1117(3)	1.2(2)	0.58(5)
Ba2	6*c*	0.068(1)	0.073(1)	0.4404(4)	1.7(2)	
Ba3	6*c*	0.067(1)	0.3288(9)	0.4441(3)	1.6(2)	
Ba4	6*c*	0.1539(7)	0.241(1)	0.0837(3)	1.5(2)	
Ba5	6*c*	0.1541(8)	0.4752(8)	0.3216(2)	3.5(2)	
Ba6	6*c*	0.1558(7)	0.2445(8)	0.2625(3)	0.8(2)	
Ba7	6*c*	0.1763(9)	0.494(1)	0.0217(2)	1.3(2)	
Ba8	6*c*	0.191(1)	0.0416(6)	0.0196(2)	1.5(1)	
Ba9	6*c*	0.2355(8)	0.4094(8)	0.1698(3)	1.4(2)	
Ba10	6*c*	0.2482(8)	0.1551(7)	0.1672(3)	0.9(2)	
Ba11	6*c*	0.2770(8)	0.6678(8)	0.2251(3)	0.6(2)	
Ba12	6*c*	0.284(1)	0.661(1)	0.1110(4)	3.6(3)	
Ba13	6*c*	0.3361(9)	0.337(1)	0.3750(1)	1.1(1)	
Ba14	6*c*	0.3397(7)	0.0792(7)	0.4375(3)	1.1(2)	
Ba15	6*c*	0.4145(8)	0.2408(8)	0.0788(2)	1.3(2)	
Ba16	6*c*	0.423(1)	0.239(1)	0.2558(2)	2.1(2)	
Ba17	6*c*	0.5027(7)	0.4164(8)	0.1687(3)	0.6(2)	
Ba18	6*c*	0.508(1)	0.150(1)	0.3538(4)	2.6(3)	
Ba19	6*c*	0.5842(8)	0.0869(7)	0.2513(3)	0.5(2)	
Ba20	6*c*	0.5894(9)	0.0897(9)	0.0675(2)	1.7(2)	
Ba21	3*b*	0.6337(5)	0	5/6	2.9(2)	
Ba22	3*a*	0.139(1)	0	1/3	2.8(3)	
Ge1	6*c*	0.500(2)	0.162(2)	0.1643(5)	0.8(2)	1.0(1)
Ge2	3*b*	0.156(2)	0	5/6	1.7(6)	
Ge3	3*a*	0.662(2)	0	1/3	1.4(2)	
O1	6*c*	0.209(5)	0.077(4)	0.0921(18)	1	0.5(2)
O2	6*c*	0.215(5)	0.457(6)	0.0938(18)		
O3	6*c*	0.328(4)	0.324(5)	0.2176(16)		
O4	6*c*	0.329(4)	0.331(5)	0.1282(12)		
O5	6*c*	0.545(5)	0.132(6)	0.4245(17)		
D1	6*c*	0.005(5)	0.284(6)	0.0453(18)	2	2.4(1)
D2	6*c*	0.000(6)	0.047(5)	0.0411(21)		
D3	6*c*	0.073(5)	0.211(6)	0.5009(18)		
D4	6*c*	0.132(5)	0.536(6)	0.1713(20)		
D5	6*c*	0.129(6)	0.541(6)	0.4244(20)		
D6	6*c*	0.208(6)	0.458(6)	0.4966(17)		
D7	6*c*	0.207(6)	0.460(6)	0.2450(21)		
D8	6*c*	0.208(7)	0.082(6)	0.2406(20)		
D9	6*c*	0.374(5)	0.049(6)	0.0470(19)		
D10	6*c*	0.400(6)	0.058(6)	0.2877(19)		
D11	6*c*	0.611(6)	0.266(6)	0.2887(20)		
D12	6*c*	0.605(6)	0.282(6)	0.0461(23)		
D13	6*c*	0.012(5)	0.511(5)	0.0116(14)	2	3.9(1)
D14	6*c*	0.089(6)	0.566(6)	0.0770(12)		
D15	6*c*	0.109(6)	0.567(6)	0.2619(12)		
D16	6*c*	0.140(6)	0.324(6)	0.3772(20)		
D17	6*c*	0.134(7)	0.153(6)	0.3719(20)		
D18	6*c*	0.224(5)	0.284(6)	0.4422(21)		
D19	6*c*	0.269(6)	0.389(7)	0.3172(19)		
D20	6*c*	0.321(6)	0.528(6)	0.3735(24)		
D21	6*c*	0.334(5)	0.163(4)	0.3297(18)		
D22	6*c*	0.420(7)	0.305(5)	0.4356(20)		
D23	6*c*	0.476(6)	0.381(6)	0.3103(20)		
D24	6*c*	0.523(6)	0.330(6)	0.3679(22)		

[a] Heavy-atom positions are from X-ray data refinement of the protide; the oxygen and deuterium parameters come from neutron data refinement. [b] X-ray study: refined isotropic displacements or fixed values used for groups of atoms. [c] Isotropic values refined from neutron data for the five groups of atoms (Ba, Ge, O, 5- and 6-coordinate D, 4-coordinate D).

the truncated tetrahedron shaded. The polyhedron defined by the last four atoms, which are the troubled Ba3 in the cubic model, is well centered by Ba13, but the edges of the large tetrahedron now range from 6.73 to 7.70 Å. The symmetry of the deuterium polyhedron within is very low (C_1).

To generate the overall structure in terms of these spheres, Figure 2C, pairs of A, A′ units are linked along $\vec{c}$ via a shared Ge3 atom that lies on a 2-fold axis, and these are connected to the B units in the same string by common trigonal Ba6−Ba16−Ba20 basal faces. Likewise, units B and B′ share the Ba21 atom on a 2-fold axis. Because this structure has a pseudocubic symmetry, similar connection patterns can be found in three other orientations. The more nearly horizontal connections between A and B units are accomplished by 12 deuterium atoms (D1−D12) in A that lie outside the surface of B and the

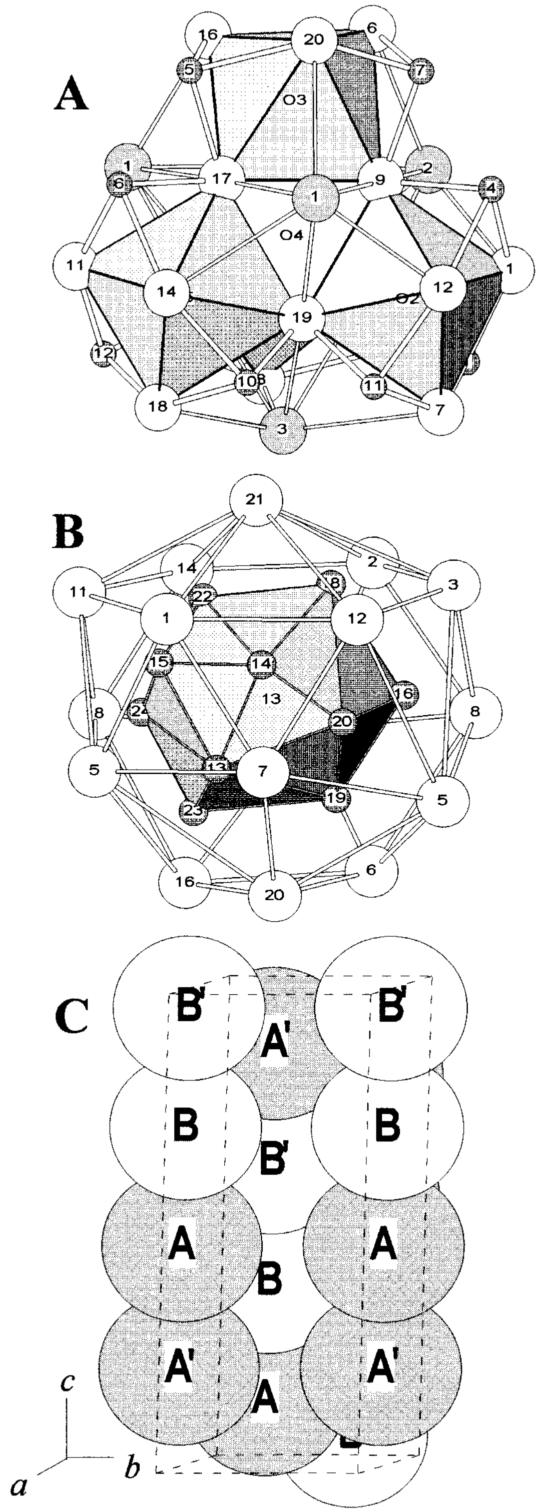

Figure 2. Building spheres that make up the $Ba_{21}Ge_2O_5D_{24}$ structure. (A) the O4-centered “hard” component; (B) the “soft” Ba13-centered deuteride component with surrounding cations. (C) The A,B composite that makes up the structure. (Primes represent spheres rotated by horizontal 2-fold axes.) Key: Ba, large open circles; Ge, large shaded circles; D, small shaded circle; O, hidden.

Table 5. Important Distances (Å) around Ba, Ge, and O Atoms in $Ba_{21}Ge_2O_5D_{24}$

Ba1−D14	2.51(6)	Ba8−D17	2.59(9)	Ba14−D6	2.93(7)	Ba22−D8 2×	3.45(7)
Ba1−D15	2.69(7)	Ba8−D16	2.71(8)	Ba14−O5	2.70(5)	Ge1−Ba17	3.56(2)
Ba1−D4	2.73(7)	Ba8−D9	2.76(7)	Ba15−D9	2.76(7)	Ge1−Ba10	3.58(2)
Ba1−D1	2.80(7)	Ba8−D2	2.83(7)	Ba15−D12	2.76(7)	Ge1−Ba17	3.65(2)
Ba1−D7	2.80(7)	Ba8−D1	2.84(7)	Ba15−O1	2.75(5)	Ge1−Ba15	3.65(2)
Ba1−D4	2.89(7)	Ba8−D2	2.89(7)	Ba15−O4	2.80(5)	Ge1−Ba19	3.66(2)
Ba1−O2	2.76(7)	Ba8−O1	2.60(6)	Ba15−O5	2.87(5)	Ge1−Ba12	3.72(3)
Ba1−Ge2	3.87(2)	Ba8−Ge3	3.76(3)	Ba15−Ge3	3.530(9)	Ge1−Ba9	3.73(2)
Ba2−D17	2.65(8)	Ba9−D7	2.84(7)	Ba15−Ge1	3.65(2)	Ge1−Ba16	3.76(2)
Ba2−D18	2.74(7)	Ba9−D4	2.88(6)	Ba16−D23	2.63(7)	Ge1−Ba11	3.81(2)
Ba2−D8	2.80(8)	Ba9−O4	2.60(5)	Ba16−D10	2.71(8)	Ge1−Ba3	3.86(2)
Ba2−D2	2.88(7)	Ba9−O3	2.79(6)	Ba16−D11	2.79(8)	Ge1−Ba20	3.97(2)
Ba2−D3	2.90(7)	Ba9−O2	2.82(6)	Ba16−D8	2.83(8)	Ge1−Ba14	4.16(2)
Ba2−D3	2.93(7)	Ba9−Ge2	3.53(2)	Ba16−D21	2.87(6)	Ge2−Ba4 2×	3.506(9)
Ba2−O1	2.67(6)	Ba9−Ge1	3.73(2)	Ba16−D5	2.90(8)	Ge2−Ba9 2×	3.53(2)
Ba2−Ge2	3.89(2)	Ba10−D8	2.75(7)	Ba16−O3	2.62(6)	Ge2−Ba10 2×	3.58(2)
Ba3−D16	2.61(7)	Ba10−D3	2.85(6)	Ba16−Ge1	3.76(2)	Ge2−Ba2 2×	3.86(2)
Ba3−D18	2.65(8)	Ba10−O4	2.59(5)	Ba17−D5	2.81(7)	Ge2−Ba1 2×	3.87(2)
Ba3−D3	2.66(7)	Ba10−O3	2.76(6)	Ba17−D6	3.09(6)	Ge2−Ba6 2×	3.91(1)
Ba3−D6	2.70(7)	Ba10−O1	2.83(6)	Ba17−O4	2.60(6)	Ge3−Ba15 2×	3.530(9)
Ba3−D9	2.79(7)	Ba10−Ge1	3.58(2)	Ba17−O3	2.78(6)	Ge3−Ba19 2×	3.55(2)
Ba3−D5	2.81(8)	Ba10−Ge2	3.58(2)	Ba17−O5	2.93(6)	Ge3−Ba4 2×	3.75(2)
Ba3−O1	2.63(7)	Ba11−D15	2.48(7)	Ba17−Ge1	3.56(2)	Ge3−Ba8 2×	3.76(3)
Ba3−Ge1	3.86(2)	Ba11−D22	2.56(9)	Ba17−Ge1	3.65(2)	Ge3−Ba18 2×	3.86(3)
Ba4−D1	2.85(7)	Ba11−D7	2.73(7)	Ba18−D24	2.54(8)	Ge3−Ba7 2×	4.05(3)
Ba4−D2	2.97(7)	Ba11−D12	2.74(7)	Ba18−D21	2.74(6)	O1−Ba8	2.60(6)
Ba4−O4	2.69(6)	Ba11−D4	2.76(7)	Ba18−D10	2.75(7)	O1−Ba3	2.63(7)
Ba4−O2	2.80(7)	Ba11−D24	2.88(8)	Ba18−D11	2.80(7)	O1−Ba2	2.67(6)
Ba4−O1	2.86(7)	Ba11−D6	2.97(7)	Ba18−D10	2.89(8)	O1−Ba15	2.75(5)
Ba4−Ge2	3.506(9)	Ba11−O5	2.62(7)	Ba18−D12	2.94(8)	O1−Ba10	2.83(6)
Ba4−Ge3	3.75(2)	Ba11−Ge1	3.81(2)	Ba18−O5	2.59(6)	O1−Ba4	2.86(7)
Ba5−D19	2.52(7)	Ba12−D14	2.72(7)	Ba18−Ge3	3.86(3)	O2−Ba12	2.66(7)
Ba5−D13	2.58(7)	Ba12−D5	2.74(7)	Ba19−D11	2.75(7)	O2−Ba19	2.66(6)
Ba5−D24	2.70(7)	Ba12−D20	2.80(8)	Ba19−D10	2.79(7)	O2−Ba7	2.72(6)
Ba5−D15	2.74(4)	Ba12−D11	2.81(7)	Ba19−O2	2.66(6)	O2−Ba1	2.76(7)
Ba5−D20	2.81(8)	Ba12−D6	2.86(8)	Ba19−O4	2.69(4)	O2−Ba4	2.80(7)
Ba5−D7	2.85(7)	Ba12−D4	2.94(7)	Ba19−O5	2.89(7)	O2−Ba9	2.82(6)
Ba5−D1	2.86(7)	Ba12−O2	2.66(7)	Ba19−Ge3	3.55(2)	O3−Ba16	2.62(6)
Ba5−D16	2.86(7)	Ba12−Ge1	3.72(3)	Ba19−Ge1	3.66(2)	O3−Ba6	2.67(6)
Ba5−D23	2.88(7)	Ba13−D19	2.52(6)	Ba20−D19	2.61(8)	O3−Ba10	2.76(6)
Ba6−D19	2.72(8)	Ba13−D13	2.52(6)	Ba20−D12	2.77(8)	O3−Ba17	2.78(6)
Ba6−D1	2.75(7)	Ba13−D22	2.61(8)	Ba20−D7	2.79(7)	O3−Ba20	2.78(6)
Ba6−D2	2.80(7)	Ba13−D14	2.63(4)	Ba20−D23	2.82(7)	O3−Ba9	2.79(6)
Ba6−D7	2.88(7)	Ba13−D16	2.74(7)	Ba20−D9	2.95(6)	O4−Ba10	2.59(5)
Ba6−D8	2.90(8)	Ba13−D18	2.76(7)	Ba20−D13	3.01(6)	O4−Ba9	2.60(5)
Ba6−O3	2.67(6)	Ba13−D24	2.76(8)	Ba20−D5	3.01(7)	O4−Ba17	2.60(6)
Ba6−Ge2	3.91(1)	Ba13−D15	2.78(5)	Ba20−O3	2.78(6)	O4−Ba4	2.69(6)
Ba7−D13	2.52(6)	Ba13−D17	2.80(8)	Ba20−Ge1	3.97(2)	O4−Ba19	2.69(4)
Ba7−D20	2.56(8)	Ba13−D20	2.87(7)	Ba21−D22 2×	2.69(7)	O4−Ba15	2.80(5)
Ba7−D14	2.79(4)	Ba13−D23	2.90(7)	Ba21−D18 2×	2.71(6)	O5−Ba18	2.59(6)
Ba7−D12	2.86(7)	Ba13−D21	2.97(5)	Ba21−D4 2×	2.88(6)	O5−Ba11	2.62(7)
Ba7−D11	2.89(8)	Ba14−D8	2.81(8)	Ba21−D6 2×	3.16(6)	O5−Ba14	2.70(5)
Ba7−D1	2.91(7)	Ba14−D3	2.83(7)	Ba22−D21 2×	2.61(6)	O5−Ba15	2.87(5)
Ba7−D9	3.01(7)	Ba14−D10	2.87(7)	Ba22−D17 2×	2.63(7)	O5−Ba19	2.89(7)
Ba7−O2	2.72(6)	Ba14−D22	2.86(7)	Ba22−D2 2×	2.82(7)	O5−Ba17	2.93(6)

germanium atoms (Figure 2) that share common cations. The more horizontal B,B′ region is that portion which was described as "metal-like" in $Ba_{21}Ge_2O_5$ etc.[4]

As far as anion sites, each oxygen atom in the structure is surrounded by six barium atoms in nearly regular octahedra with O−Ba distances between 2.59 and 2.93 Å. Germanium anions are surrounded by 12 barium atoms in deformed icosahedra with a average separation of 3.72 Å. Deuterium anions exert the least influence on their environment and so occupy interstices defined by generally distorted tetrahedral, square-pyramidal, and octahedral barium polyhedra with various bond distances (2.70−3.15 Å in first group, 2.5−3.0 Å in second; $\sigma = 0.06-0.09$ Å). Bond order sums[23] about deuterium and oxygen atoms are generally close to the expected values of 1.0 and 2.0, respectively, Table 6.

Properties. An oxidation state count for the $Ba_{21}Ge_2O_5H_{24}$ structure indicates it is compositionally and structurally electron-precise and is thus a Zintl phase, i.e., $21(Ba^{+2}) + 2(Ge^{-4}) + 5(O^{-2}) + 24(H^{-})$ in oxidation states. The electronic conduction and magnetic properties are both consistent with this assignment. The expected semiconducting (or insulating) behavior was confirmed by "Q" measurements, which gave a minimum resistivity at room temperature of 3 mΩ·cm. As illustrated in Figure 4, the compound is diamagnetic with $\chi_M \sim -7.0 \times 10^{-5}$ emu·mol^{-1} over about 50−300 K after correction for core contributions.

Crystallographic and Other Results. The original studies by Röhr reported that $Ba_{21}Ge_2O_5$ and four other analogues

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(23) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192.

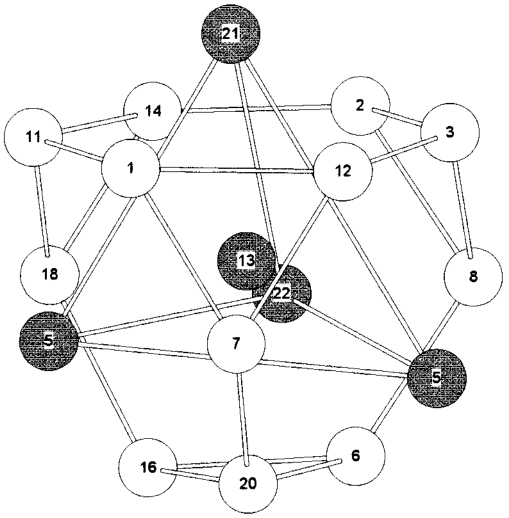

Figure 3. The Ba_{16} polyhedron and the centering Ba13 in the B sphere (inverted). This is close to a tetracapped truncated tetrahedron in which the approximate tetrahedron of capping atoms (shaded) are equivalent to the troubled Ba3 atoms in the cubic approximation.

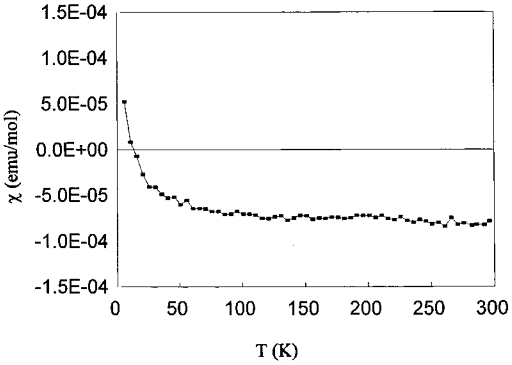

Figure 4. Molar magnetic susceptibility of single-phase $Ba_{21}Ge_2O_5H_{24}$ as a function of temperature at a 3 T field.

Table 6. O−Ba and D−Ba Bond Order Sums in $Ba_{21}Ge_2O_5D_{24}$

O1−6Ba	1.92	D11−5Ba	1.03
O2−6Ba	1.82	D12−5Ba	1.02
O3−6Ba	1.84	D13−4Ba	1.40
O4−6Ba	2.24	D14−4Ba	1.26
O5−6Ba	1.77	D15−4Ba	1.24
D1−6Ba	1.15	D16−4Ba	1.04
D2−6Ba	1.06	D17−4Ba	1.22
D3−5Ba	0.99	D18−4Ba	1.06
D4−6Ba	1.13	D19−4Ba	1.50
D5−5Ba	0.93	D20−4Ba	0.98
D6−5Ba	0.81	D21−4Ba	0.90
D7−6Ba	1.21	D22−4Ba	1.21
D8−5Ba	1.00	D23−4Ba	0.86
D9−5Ba	0.94	D24−4Ba	1.09
D10−5Ba	1.06		

crystallize with face-centered-cubic symmetry, space group $Fd\bar{3}m$, which can be transformed into a rhombohedral cell with $\alpha \sim 60°$. However, the results of the structure determinations for Ge and Si were unusual, particularly with respect to the Ba3 atoms (16*d*: $^1/_2$, $^1/_2$, $^1/_2$; etc.) which showed unusually large thermal parameters, $U_{iso} = 0.183(8)$ Å^2 in the germanium example relative to ≤ 0.018 Å^2 for the other cations and a maximum of 0.036(3) Å^2 for Ba here. Precession photographs of the cubic cell were taken, but no superstructure reflections were mentioned. During X-ray diffractometer work, we found some relatively strong reflections that required a primitive trigonal cell. Subsequently, additional trigonal reflections in the *hk*1 and *hk*2 precession films taken along the 3-fold axis direction confirmed this assignment. None of these additional trigonal reflections can be observed by Guinier powder diffraction, the stronger ($\leq$8.7% of I_{max}) because of overlap with strong 2θ-equivalent cubic data, while the strongest resolvable trigonal datum is only 0.7% I_{max}.

The difficulties with the trigonal refinements stem from the pseudocubic symmetry. The fraction of reflections observed ($3\sigma_I$) in the primitive trigonal setting is quite low, about 22%, and 90% of them belong to the cubic substructure. Anisotropic parameters of all of the heavy atoms could not be refined because of the quality and quantity of the X-ray data vs the number of variables. Refinement of the neutron data on the face-centered-cubic model was even more troublesome than found with the X-ray data set. One of the two deuterium atoms (D2) had a very large thermal parameter, implying that the real position differs very much from that model. Some additional weak reflections could also be observed in the neutron pattern because of the relatively high neutron scattering factor of deuterium, which atoms contribute about 50% of the total diffracted intensity.

A group−subgroup relationship exists between the ideal cubic, the rhombohedral, and the primitive trigonal cells: $Fd\bar{3}m \rightarrow Fd\bar{3} \rightarrow F23 \rightarrow R32 \rightarrow P3_121$. X-ray refinements in space groups from $Fd\bar{3}m$ to *R*32 showed that their atomic positions and thermal parameters are not significantly different. However, the symmetry change from *R*32 to $P3_121$ produces about 10% more observed X-ray reflections (from a cell with 75% of the cubic volume) as every atom in the *R*-type symmetry splits into three in primitive trigonal symmetry. The principal difference between the two space groups is the conversion of the proper 3-fold axis along the $\vec{c}$ direction (hexagonal setting) into an improper rotation axis together with the loss of some perpendicular 2-fold axes (proper and improper). (The atom arrangements in the trigonal structure are described in some detail in the Supporting Information by seven sections of the structure along $\vec{c}$.)

A simple way to contrast the solutions for the two cells is in terms of the atom deviations from the 3-fold axes in the rhombohedral structure, trigonal setting (along $^1/_3$, $^2/_3$, *z*; etc.). Here the order on the axis is Ge3 → O4 → O3 → Ba13 → Ba21 → Ba13 → O3 → O4 → Ge3, there being a perpendicular 2-fold axis through the central Ba21. The deviations of most atoms from this in the real structure are very small (within 3σ), 0.08 Å for Ge3, 0.05 Å for O4, 0.12 Å for O3, and 0.06 Å for Ba13, but the Ba21 atoms, which correspond to parts of the troubled Ba3 atom in the fcc structure (16*d*: $^1/_2$, $^1/_2$, $^1/_2$; etc.), have moved away from the 3-fold axis by 0.60 Å. Of course, differences between the two entire structures include displacements of other atoms surrounding this axis as well.

Deuterium atoms D13−D24, which would correspond to the single D2 type in the cubic structure, are very much different from the single placement. In the fcc structure, a D2 atom polyhedron centered by a Ba4 atom (trigonal Ba13) has the form of a cuboctahedron with T_d symmetry. However, the D−Ba distances therein would be much too short (<2.47 Å) in all three possible cubic groups, and such a lack of suitable cavities for deuterium in this symmetry must in fact lead to the distortion of this polyhedron and of the structure. This is the nature of sphere B, Figure 2. On the other hand, oxygen and germanium center high coordination barium polyhedra that are relatively “rigid” or “hard” because of their higher formal charges (sphere A, Figure 2). This dominant heavy-atom arrangement plays a key role in the formation of the pseudo-fcc structure. In contrast, the low-field, polarizable deuterium atoms (B) are relatively "anomalous"[24] or "soft"[25] and end up in a variety (24) of barium environments. These seem to be more responsible for the adoption of the primitive trigonal symmetry.

The formation of pseudo-fcc structures for the three compounds $Ba_{21}Tr_2O_5H_x$, Tr = Ga In, Tl, has also been verified by single-crystal X-ray diffraction in parallel with the studies on the Ge compound. The isotypic primitive trigonal cell for the Ga example has also been confirmed on the diffractometer, but not yet for Si, In, Tl. In cubic refinement attempts, certain barium atoms again have troublesome thermal parameters, and similar problems may have prevented the identification of Ba4 and thence the correct heavy-atom composition of "$Ba_{10}Ga$" from precession film data.[3] According to the Zintl -phase concepts, the trielide compounds should contain only 22 hydrogen atoms per formula and be constituted as $(Ba^{+2})_{21}(Tr^{-5})_2(O^{-2})_5(H^-)_{22}$. The high cation field may help stabilize the closed-shell state Tr^{-5} and therefore ensure the full quota of 22 H^-, but this has not been verified for any of the trielides.

The 1957 report of the structure of cubic $Al_{10}V$[26] shows that it has a close relationship not only to that of "$Ba_{10}Ga$"[3] but also to the present pseudocubic $Ba_{21}T_2O_5H_x$ phases. Aluminum occupies the cubic Ba1,2,3 (but reportedly not the Ba4) type sites, with vanadium in idealized Ga 16*c* positions within aluminum icosahedra. The $Al_{10}V$ result is unusual in three respects: a strikingly large atomic volume per atom; empty aluminum octahedra; large, empty 16-atom aluminum polyhedra (Figure 3) where cubic Ba4 (trigonal Ba13) is found here. The second and third cavities are suitably sized for O and Al, respectively. A redetermination of the structure seems necessary to establish (at least) the correct aluminum and any oxygen content. Likewise, a novel $Ba_{17}Al_3O_7$ was recently reported[27] that exhibits some of the same themes found in $Ba_{21}T_2O_5$, particularly a metal-like region with large Ba−Ba distances (>4.43 Å) between Al−O−Ba clusters. This may again mean hydride involvement. The compound seems especially interesting because of the implications of both oxoaluminate (Al^{+3}) and aluminide (Al^{-5}) components, for which a clear hydride count would be especially meaningful should it be electronically closed-shell.

Acknowledgment. We are indebted to S. Short and J. Jorgensen for provision of the neutron diffraction data and to J. E. Ostenson for the magnetic measurements. This research has benefited from the use of the Intense Pulsed Neutron Source at Argonne National Laboratory, which is funded by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

Supporting Information Available: Tables giving more details of the data collection and refinement for $Ba_{21}Ge_2O_5H_{24}$ and distances within the polyhedra about each D atom and a figure showing seven [001] sections of the trigonal structure (5 pages). Ordering information is given on any current masthead page.

IC971339Y

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