cuss such minor bond-length variations.[28] The V_2O_8 group in CsV_3O_8 is only slightly distorted from the ideal form shown in Figure 3b. If a plane is passed through the outer oxygen atoms numbered 2, 5′, 5″, and 2′ (Figure 4), the central oxygen atoms 3 and 3′ are displaced from the plane 0.15 A. The V_2 atoms lie 0.52 A from this plane, and the bonds V_2–O_4 make an angle of 87.5° with the plane.

The double V_2O_8 group illustrated in Figure 3b now appears to be a characteristic feature of many oxovanadium(V) structures. It can be clearly discerned in LiV_3O_8,[21] V_2O_5,[22] and $Na_3V_6O_{15}$.[23] Its discrete character is strikingly emphasized by its appearance in isolated form (but linked through UO_2^{2+} groups into a sheet structure) in the crystal structure of the carnotite analog $Cs_2(UO_2)V_2O_8$.[36] A binucleate ion $HV_2O_7^{3-}$ has been identified by Ingri and Brito[8,9] in alkaline vanadate solutions. This ion may be formulated $H_3V_2O_8^{3-}$, but of course it is not possible at this time to say whether it corresponds to the V_2O_8 group in the solid compounds. The V_2O_8 group is wholly lacking in the $V_{10}O_{28}^{6-}$ ion.[25] It is possible that the slow formation of KV_3O_8 from solutions of $V_{10}O_{28}^{6-}$ may be a result of some complex intermediate reactions in which the creation of the V_2O_8 group is involved.

A final detail worth noting is the close approach of the bridging oxygen atoms in the V_2O_8 group, namely, 2.30 ± 0.02 A in CsV_3O_8. This is fairly consistent with the distance of 2.35 ± 0.05 A found for the corresponding pair of atoms in $Cs_2(UO_2)V_2O_8$,[36] 2.42 ± 0.04 A found in LiV_3O_8,[21] 2.388 ± 0.003 A in V_2O_5,[22] and 2.43 ± 0.05 A in $Na_3V_6O_{15}$.[23] A pair of bridging oxygen atoms between two highly charged cations is frequently drawn quite close together. Between octahedrally coordinated aluminum in aluminosilicates, for example, this distance often lies between 2.4 and 2.5 A. The distances found in the V_2O_8 groups seem to be unusually short. Nevertheless, the shortest distance of this type that has been reported so far was found by Burnham and Buerger[37] in andalusite (Al_2SiO_5) for a pair of oxygen atoms bridging two aluminum atoms in fivefold coordination, namely, 2.247 ± 0.007 A.

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Notes

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Preliminary Crystallographic Studies on the Systems Calcium–Lanthanum–Hydrogen and Calcium–Yttrium–Hydrogen

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Solid solutions of yttrium trifluoride in calcium fluoride have been known since 1914[2] and have recently been definitely characterized by Short and Roy.[3] Up to 55 mole % YF_3 enters the fluorite lattice, the extra F^- of YF_3 entering the octahedral holes of CaF_2 until these are filled at a nominal 50%. The crystallographic analogy of hydride ion in saline hydrides to fluoride ion suggested the investigation of corresponding calcium–rare earth–hydrogen systems. Lanthanum and yttrium were chosen for first investigation by virtue of differing ionic size; the Zachariasen[4] ionic radii are: Ca^{2+}, 0.94 A; La^{3+}, 1.04 A; Y^{3+}, 0.88 A. CaH_2 is orthorhombic;[5] lanthanum forms an fcc fluorite phase from (approximately) LaH_2 through LaH_3;[6] YH_2 is fcc fluorite and YH_3 is hexagonal.[7] All of these are nonstoichiometric to some extent.

Experimental Section

The calcium metal was obtained from Dominion Magnesium, Ltd., Toronto, Canada, 99.9%. Lanthanum was obtained from Cerium Metals Division of Ronson Metals, Inc., Newark, N. J., 99+%. Yttrium was obtained from United Mineral and Chemical Co., New York, N. Y., 99+%.

The metals were weighed out into molybdenum boats in an argon glove box and allowed to react with catalytically purified hydrogen at elevated temperatures. The amount of hydrogen taken up was determined by $P-V-T$ measurements. Each sample was ground to powder in an agate mortar in the argon drybox, and a sample was withdrawn for X-ray powder crystallography. The bulk of the sample was returned to the hydrogen reaction system, where it was further exposed to measured hy-

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drogen with the same time–temperature cycle as the first treatment. After regrinding, a second X-ray sample was taken. In all cases, only small changes were produced by the second hydrogen treatment.

The X-ray powder patterns were taken in part with a General Electric XRD-4 unit and 143.2-mm camera and in part with a Norelco diffractometer, Type 12045, and 114.6-mm camera. Cu Kα radiation with a Ni filter and 0.3–0.5-mm glass capillaries were used. Standard film exposure time was 5 hr. The amounts of the phases present were based on visual judgment of the intensities of certain characteristic lines, as compared with the intensities of the same lines for $CaH_{1.88}$ and $LaH_{2.66}$. Lattice constants of the fcc phases were determined by Nelson–Riley extrapolations to $\theta = 90°$, except in one case (see Table I) where the lines of higher indices were so diffuse that reliable extrapolation was not possible.

Two types of sample were prepared: (a) of attempted limiting over-all composition $Ca_xR_{1-x}H_{3-x}$ and (b) of attempted composition $Ca_xR_{1-x}H_2$. In (a), after reacting at temperatures up to 700°, the samples were kept at 400° for La and 300° for Y for 1 hr, followed by slow cooling in contact with hydrogen to room temperature. In (b), after treatment at 700° for 1 hr, the samples were cooled rapidly, with the stopcock between sample bomb and system closed to minimize further hydrogen uptake.

Results

Lanthanum.—The results for lanthanum are shown in Table I. The lines of orthorhombic CaH_2 are missing or weak in the samples containing 40 and 60% Ca, and relatively weak at higher calcium contents. The lines of the face-centered-cubic phase persist at relatively high intensities up to the highest Ca contents.

TABLE I

CALCIUM–LANTHANUM–HYDROGEN RESULTS[a]

Sample composition	Ortho-rhombic phase	Face-centered-cubic phase	Lattice const, a_0, A, fcc
Equilibration at 400°; Slow Cooling to 25°			
$LaH_{2.66}$	. . .	s	5.623 ± 0.004
$Ca_{0.40}La_{0.60}H_{2.30}$	vvw	s	5.600 ± 0.004
$Ca_{0.61}La_{0.39}H_{1.84}$	None	ms	5.619 ± 0.004
$Ca_{0.70}La_{0.30}H_{2.17}$	mw	m	Diffuse
$Ca_{0.82}La_{0.18}H_{2.15}$	ms	m	5.629 ± 0.004
$Ca_{0.90}La_{0.10}H_{1.86}$	m	m	5.638 ± 0.004
$CaH_{1.88}$	s	. . .	. . .
Equilibration at 700°; Rapid Cooling in Isolation from H_2			
$LaH_{2.18}$	. . .	s	5.672 ± 0.004
$Ca_{0.40}La_{0.60}H_{2.28}$	w	ms	5.626 ± 0.002
$Ca_{0.61}La_{0.39}H_{1.90}$	w	ms	5.616 ± 0.002
$Ca_{0.70}La_{0.30}H_{2.08}$	mw	m	5.64 ± 0.01
$Ca_{0.82}La_{0.18}H_{1.70}$	m	m	5.639 ± 0.004
$CaH_{1.88}$	s	. . .	. . .

[a] s, strong; m, medium; w, weak.

The control of the hydrogen content by thermal treatment was not as effective as planned. The second series, equilibrated at 700°, contained only a little less hydrogen than the first 400° series, and the difference was irregular. Thus, the amounts and compositions of the phases present are probably not equilibrium values.

The lattice constants of the orthorhombic phase shown in Table II were calculated from data for five of the Ca–La–H samples as well as from one pure CaH_2 pattern. There was no correlation with composition, but the values from the La-containing samples averaged lower than those for the pure CaH_2 samples.

TABLE II

CALCIUM HYDRIDE LATTICE CONSTANTS, A

	a_0	b_0	c_0
Samples with La (this research)	5.93 ± 0.01	3.604 ± 0.005	6.82 ± 0.03
Pure CaH_2 (this research)	6.00	3.615	6.85
Pure CaH_2 (ref 5)	5.936	3.600	6.838

Yttrium.—These results are in Table III. Control of the hydrogen content was successful here. The orthorhombic CaH_2 phase was present with stronger line intensities than in the La samples of corresponding composition. The fcc YH_2 phase predominated in the low-hydrogen series, and the hexagonal YH_3 phase predominated in the high-hydrogen series. The amounts of hexagonal phase in the low-hydrogen series were anomalously high. No trend of lattice constants with composition was observed.

TABLE III

CALCIUM–YTTRIUM–HYDROGEN RESULTS

Sample compositions	Orthorhombic phase	Hexagonal phase	Fcc phase
Equilibration at 300°; Slow Cooling in H_2			
$Ca_{0.30}Y_{0.70}H_{2.45}$	vvw	ms	vvw
$Ca_{0.45}Y_{0.55}H_{2.35}$	w	ms	vw
$Ca_{0.60}Y_{0.40}H_{2.16}$	m	ms	. . .
Equilibration at 750°; Rapid Cooling in Isolation from H_2			
$Ca_{0.30}Y_{0.70}H_{1.96}$	vw	w	vs
$Ca_{0.45}Y_{0.55}H_{1.97}$	vw	m	s
$Ca_{0.60}Y_{0.40}H_{1.95}$	m	mw	s

Lattice Constants

$$\text{Hexagonal}\begin{cases} a_0 = 3.68 \pm 0.01\ \text{A},\ c_0 = 6.61 \pm 0.01\ \text{A (this research)} \\ a_0 = 3.674\ \text{A},\ c_0 = 6.599\ \text{A (ref 7)} \end{cases}$$

$$\text{FCC}\begin{cases} a_0 = 5.210 \pm 0.005\ \text{A (this research)} \\ a_0 = 5.201\ \text{A (ref 7)} \end{cases}$$

Discussion

In the yttrium samples, the phases present were those to be expected in a mechanical mixture of the same over-all composition and assuming no interaction, with the exception that the hexagonal YH_3 phase was found in the low-hydrogen samples. The hysteresis in the formation and decomposition of YH_3[8] might be related to the persistence of this phase.

In the lanthanum samples, the lattice constants correlate with the mole percentages of calcium in the metallic portions of the preparations, as shown in Figure 1, with one anomalous point. In both series, increasing amounts of Ca result in increasing lattice constants. In both series, the lattice constants do not extrapolate to the appropriate values for LaH_2 and LaH_3. This would suggest that the fcc phase is different from ordinary fcc LaH_x, the presence of Ca^{2+} perhaps producing a different defect array so that the lattice constant depends more on the amount of Ca^{2+} than on the amount of hydrogen present.

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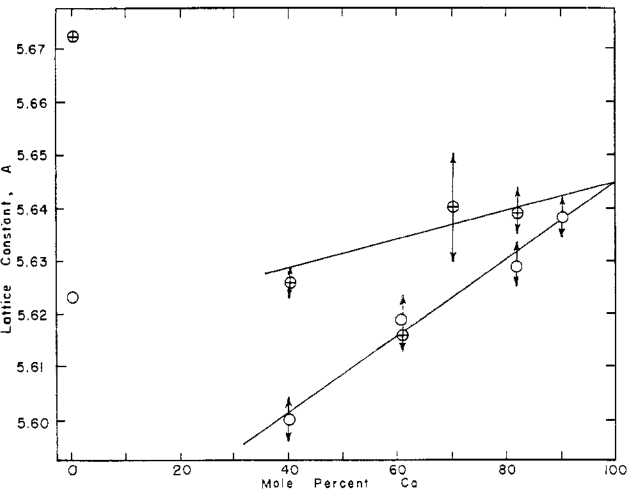

Figure 1.—Lattice constant *vs.* mole per cent calcium in metallic content, Ca–La–H samples: ○, series equilibrated at 400°; ⊕, series equilibrated at 700°.

Warf and Hardcastle[9] have demonstrated the existence of two face-centered-cubic forms of ytterbium hydride, prepared by allowing metal to react with H_2 at pressures above 1 atm. One of these has a composition of approximately $YbH_{2.5}$. The other, prepared by thermal decomposition of the first, is metastable at ordinary pressure and temperature in a sample of as low a hydrogen content as $YbH_{2.04}$.

In the process of adding hydrogen to YbH_2, conduction electrons would be released, and some Yb^{2+} would be changed to Yb^{3+}. The addition of lanthanum hydride to CaH_2 would produce La^{3+} and conduction electrons which might achieve the same effect. It should be noted that it is precisely the two rare earth dihydrides with few conduction electrons—YbH_2 and EuH_2—which are orthorhombic, while all others are cubic. The formation of the higher hydride of ytterbium indicates that the energy difference between the two structures may not be large, so that the conduction electrons or the additional lattice energy from the R^{3+} might produce the change.

It should be noted that CaH_2 undergoes a transition on heating at 780°,[10,11] to a phase of undetermined structure, possibly fcc.

Since the samples are not equilibrium samples, the possibility of no interaction must be examined. This would require that the observed fcc lattice constant would indicate how much of the total hydrogen was combined with La, the rest being combined with Ca. If this is done, using the closely agreeing lattice constants of Korst and Warf[12] and Goon,[13] the calculated compositions give the difficulty that, in most of the samples of Table I with less than two atoms of H per atom of La, there would be insufficient hydrogen to react with all of the Ca. There is no indication of uncombined Ca in the X-ray patterns, but again the amounts might be too small to detect.

Another assumption, in accord with the free energies of formation of CaH_2[11] and LaH_2,[12] would be that on combination hydrogen would first form LaH_2, then CaH_2. If any remained, it would react further with LaH_2. The number of gram-atoms of H combined with 1 g-atom of La, calculated in this way for each sample, does not correlate with the lattice constants of the fcc phase. There is a scattering of points, rather than the linear relationship of the literature results[12,13] in the absence of Ca. A lattice constant independent of the H to La ratio would again indicate a structural change in LaH_x caused by the presence of Ca.

No conclusions about the nature of the fcc phase in the Ca–La–H system may be drawn from this research, but interaction to form a novel phase is probable.

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The Thermal Decomposition of Copper(II) Chelates of N-Substituted Thiopicolinamides

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In a previous study involving copper(II) chelates of N-substituted thiopicolinamides, the anomalous melting behavior of bis-(N-benzylthiopicolinamidato)-copper(II) (**1**) was observed.[1] This effect has now been more fully studied and found to involve the thermal reduction of the copper(II) chelate in part to the corresponding copper(I) chelate.

Experimental Section[2]

Thermal Decomposition of Bis-(N-benzylthiopicolinamidato)-copper(II).—Bis-(N-benzylthiopicolinamidato)copper(II) (0.211 g, 0.407 mmole, red-brown needles, mp 161° dec, $\mu = 1.83$ BM) was heated at 150° (0.2 mm) for 5 hr to yield a condensate of pure N-benzylthiopicolinamide (0.092 g, 0.403 mmole), identified by mixture melting point, infrared spectrum, and proton nmr spectrum, and a diamagnetic rust-colored residue (0.117 g, 99% of the residue expected, based on the loss of one molecule of N-benzylthiopicolinamide). Comparable results were observed for disproportionations carried out for varying times at temperature as low as 120°, although the residue obtained varied slightly from condition to condition. *Anal.* Calcd for $C_{13}H_{10}CuN_2S$: C, 53.87; H, 3.48; N, 9.67. Found: C, 53.85; H, 3.72; N, 9.70.

Prolonged (2 days) shaking of the residue in 6 *N* hydrochloric acid in the presence of air gave an insoluble green product which

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[2] All temperatures are uncorrected. Nmr resonances are in ppm relative to tetramethylsilane as an internal standard, downfield being considered the negative direction.