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The crystal structure of calcium hydride.*

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The crystal structure of the earth–alkali hydrides was studied by Zintl & Harder (1935) who found that calcium, strontium and barium hydride are isomorphous. As far as the metal ions are concerned these structures could be described as follows.

Space group *Pnma*, 4 units MH_2 per cell;
for calcium hydride
$a = 5{\cdot}936$, $b = 3{\cdot}600$, $c = 6{\cdot}838$ Å;
M in 4(*c*) with $x = 0{\cdot}260$ and $z = 0{\cdot}110$.

This metal arrangement is a slightly distorted hexagonal close packing. The hydrogen atoms were assumed to occupy two 4-fold positions in 4(*c*) with parameters as given in Table 2. Half of the hydrogen atoms is situated in the centres of the octahedral holes of the calcium lattice and the other half in the centre of a triangle of three calcium ions forming the common base of two tetrahedra. This structure is related to $PbCl_2$ in cell dimensions and metal positions. However, the hydrogen positions of Zintl & Harder represent a severe distortion of the lead–chloride structure, in that in $PbCl_2$ half of the chlorine ions are surrounded tetrahedrally by lead atoms, the other half being displaced from the centres of the octahedra so that they have only five neighbours.

A neutron–diffraction investigation was undertaken to obtain more information about the positions of the hydrogen atoms. Powdered samples of calcium hydride and deuteride were prepared from the elements and diffraction patterns taken on the diffractometer described by Goedkoop (1957) using neutrons from JEEP, the reactor at Kjeller, Norway. These diagrams, with instrumental background subtracted, are shown in Fig. 1. The integrated intensities corrected for the angular dependence are tabulated in Table 1. The experimental data were in disagreement with the values calculated for the parameters suggested by Zintl & Harder (Table 1).

A geometrical analysis of the available space in the calcium structure, however, showed that the hydrogen positions of Zintl & Harder are very unlikely. All the calcium ions are in symmetry planes. From geometrical considerations it is evident that the hydrogen atoms must be situated in these same planes. With the radius of a calcium ion of 0·99 Å and a radius of the hydrogen ion of 1·31 Å around every calcium ion a sphere of radius $r_{Ca^{++}} + r_{H^-}$ could be constructed. This sphere is the locus of points where the centre of a hydrogen ion, bound to that calcium ion, might be situated. Because of the hexagonal packing of the calcium ions, in every

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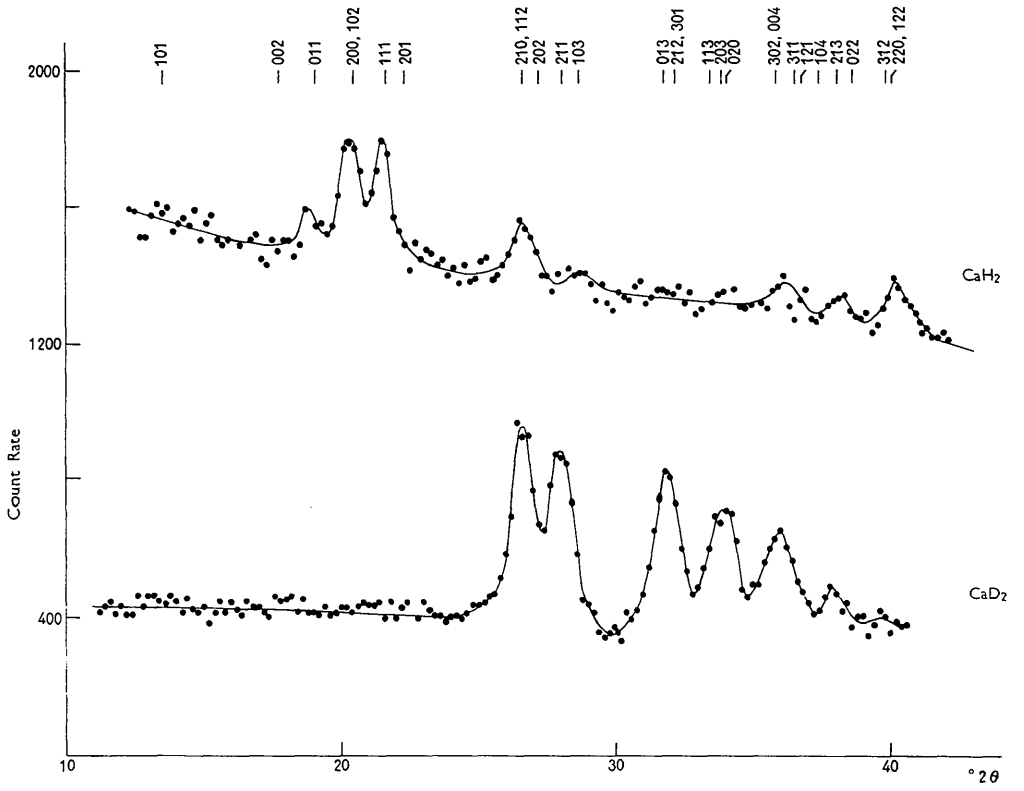

Fig. 1. Neutron diffraction patterns of CaH_2 and CaD_2, taken with $\lambda = 1{\cdot}053$ Å.

Table 1. *Observed and calculated neutron-diffraction data for calcium hydride and deuteride*

		CaD_2				CaH_2			
			Z. & H.-model	CaH_2-model	$PbCl_2$-model		Z. & H.-model	CaH_2-model	$PbCl_2$-model
hkl	2θ	jF_o^2	jF_c^2	jF_c^2	jF_c^2	jF_o^2	jF_c^2	jF_c^2	jF_c^2
101	13·49	0	0	0	0·2	0	0	0	0·1
002	17·72	0	0·1	0·4	0	0	0	0	0·1
011	19·03	0	0	0	0	1·8	2·1	1·9	1·9
200	20·44	0	1·6	0·4	0	5·9	5·3	6·8	7·0
102	20·48								
111	21·63	0	0·9	0	0	6·7	7·5	6·4	5·2
201	22·30	0	0	0·9	0·1	0	0	0	0·1
210	26·59								
112	26·62	19·8	15·5	22·6	23·3	5·8	1·6	5·5	5·2
202	27·18								
211	28·07	21·5	37·7	22·5	17·4	1·6	0·5	1·4	0·9
103	28·66								
013	31·74								
212	32·13	23·6	34·3	18·3	20·0	0	0·4	2·8	1·1
301	32·17								
113	33·41								
203	33·87	25·2	22·5	23·5	29·0	0	0·5	1·0	1·1
020	34·02								
302	35·81								
004	35·88	22·4	0·5	24·2	21·7	6·0	12·3	1·6	2·5
311	36·51								
121	36·75								
104	37·39								
213	38·05	8·3	6·7	7·0	11·2	4·0	5·1	4·0	4·7
022	38·61								
312	39·81								
220	40·02	2·4	3·4	3·5	0·4	10·9	7·3	12·2	12·9
122	40·04								
			49·5%	13·5%	17·0%		44·2%	26·4%	29·8%

symmetry plane there are points of intersection of three such spheres corresponding with hydrogen ions having equal bonds to three calcium ions. In this way a number of points is found arranged in pairs around a tetrahedral hole and in groups of four around an octahedral hole.

Table 2. *Hydrogen parameters in a few models*

	H_I		H_{II}	
	x	*z*	*x*	*z*
Zintl & Harder model	0·260	0·430	0·996	0·758
$PbCl_2$ model	0·375	0·435	0·941	0·688
CaH_2 model	0·375	0·435	0·000	0·660

By an appropriate choice of the radius of the hydrogen ion, the pairs around tetrahedral holes can be made to coincide, giving a possible hydrogen position with four equal Ca–H bonds. The octahedra do not reduce to single positions. The hydrogens could be distributed over the available sites, taking into account that the interatomic distance of two hydrogen ions should be larger than a minimum value. This condition could be satisfied in one arrangement only. The parameters so obtained are listed in Table 2. The hydrogen positions satisfy *Pnma* symmetry. The intensities calculated for this structure are given in Table 1. They are seen to agree much better with the observed values than those calculated from the Zintl & Harder model. The parameters represent a slight distortion from the structure of lead chloride. A calculation with the hydrogen atoms slightly rearranged so as to correspond with the positions occupied by chlorine in $PbCl_2$ is listed in the last columns of Table 1. As a measure of the relative merit of the calculations, at the end of every column the value of $\Sigma j|F_c^2 - F_o^2|/\Sigma j F_o^2$ has been given.

In the calculations temperature factors for hydrogen and deuterium were applied as obtained from inelastic neutron-scattering experiments (Bergsma & Goedkoop, 1960).

In the structure of calcium hydride each calcium ion is surrounded by nine hydrogen ions of which seven at 2·32 and two at 2·85 Å. Conversely, each hydrogen of type I has four calcium ions at 2·32 Å and eight hydrogen ions at distances varying between 2·50 and 2·94 Å. Each hydrogen of type II is bound to three calcium ions at 2·32 and two at 2·85 Å and ten hydrogen ions at distances between 2·65 and 3·21 Å.

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