Acta Cryst. (1979). A**35**, 818–820

Redetermination of the Neutron Scattering Length of Holmium

BY J. X. BOUCHERLE, S. QUEZEL, J. SCHWEIZER* AND F. TCHEOU
DRF/DN CENG, 85 *X*, 38041 *Grenoble CEDEX, France*

(*Received* 19 *June* 1978; *accepted* 4 *April* 1979)

Abstract

An attempt to determine accurately the neutron scattering length of holmium from Ho_2O_3 and Ho_2O_2S powders did not give accurate results. It indicated however that the currently accepted value $b_{Ho} = 8{\cdot}5 \times 10^{-12}$ mm was too high. A very precise determination was possible with a $HoAl_2$ single crystal and polarized neutrons. The new value is $b_{Ho} = 8{\cdot}08\ (5) \times 10^{-12}$ mm.

Introduction

In the course of a polarized neutron diffraction study of the Laves phase of $HoAl_2$, it was realized that the knowledge of the scattering length of holmium is rather inexact. Its value ($b = 8{\cdot}5 \times 10^{-12}$ mm) corresponds to an old experiment on the oxide Ho_2O_3 (Koehler, Wollan & Wilkinson, 1958). So a redetermination of this value was undertaken on powder samples of the oxide Ho_2O_3 and the oxysulphide Ho_2O_2S. Moreover, a combination of polarized and unpolarized neutron experiments on a $HoAl_2$ single crystal were also carried out.

Determination from powder Ho_2O_3

The oxide is easily available in high purity. This compound crystallizes in space group *Ia*3 with 16 formula units in the unit cell. The atoms occupy the following positions:

Ho(1) in 8(*b*) $\frac{1}{4},\frac{1}{4},\frac{1}{4}$; *etc.*,
Ho(2) in 24(*d*) $u,0,\frac{1}{4}$; *etc.*,
O in 48(*e*) *x*,*y*,*z*; *etc.*

A neutron diffraction pattern was obtained at room temperature with the multidetector D1B (Convert, 1975) at the ILL high-flux reactor in Grenoble. For a wavelength of 2·4 Å, 55 Bragg reflexions were recorded between $2\theta = 20$ and $2\theta = 139°$. The structural parameters were determined by a profile refinement (Rietveld, 1967, 1969; Hewat, 1973) minimizing the function

$$M = \sum_i w_i \left[y_i(\text{obs}) - \frac{1}{k}\, y_i(\text{calc}) \right]^2,$$

where k is the scale factor, $y_i(\text{obs})$ and $y_i(\text{calc})$ the observed and calculated intensities at any point and w_i the weighting factor for this point. Two reliability factors are defined. The first one, R_{pr}, concerns the profile analysis:

$$R_{\text{pr}} = \left\{ \sum_i w_i \left[y_i(\text{obs}) - \frac{1}{k}\, y_i(\text{calc}) \right]^2 \Big/ \sum_i w_i [y_i(\text{obs})]^2 \right\}^{\frac{1}{2}}$$

and the second, R_B, is based on Bragg reflexions:

$$R_B = \sum \left[F_i^2(\text{obs}) - \frac{1}{k}\, F_i^2(\text{calc}) \right] \Big/ \sum F_i^2(\text{obs}).$$

The scattering length of oxygen was taken to be $b_O = 5{\cdot}80 \times 10^{-12}$ mm and results of the refinement are reported in Table 1. The correlations between the scattering length of holmium, b_{Ho}, and the thermal parameter of the oxygen atoms B_O are too high to allow an accurate determination of the former. In this case, it is more significant to show the variation of b_{Ho} as a function of B_O (Fig. 1).

To avoid this uncertainty, we carried out a refinement of the powder pattern at $T = 4{\cdot}2$ K on the diffractometer DN3 at the reactor Siloe of the CEN,

Table 1. *Crystallographic parameters of* Ho_2O_3 *at* $T = 293$ *and* $T = 4{\cdot}2$ K

Standard deviations are in parentheses.

		x	*y*	*z*	*B* (Å²)	R_B (%)	R_{pr} (%)
293 K	Ho_I	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0·04 (24)		
	Ho_{II}	−0·0323 (3)	0	$\frac{1}{4}$	0·19 (12)	1·53	7·27
	O	0·3907 (4)	0·1520 (4)	0·3797 (5)	‡		
4·2 K	Ho_I	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0·10†		
	Ho_{II}	−0·0330 (3)	0	$\frac{1}{4}$	0·10†	1·23	13·51
	O	0·3905 (5)	0·1513 (4)	0·3800 (6)	‡		

† These parameters were not refined.
‡ Value correlated with b_{Ho} (see Fig. 1).

---

* Also: Institut Laue–Langevin, 156X, 3804 Grenoble CEDEX, France.

0567-7394/79/050818-03$01.00

Table 2. *Crystallographic parameters of* Ho_2O_2S *and scattering length of holmium*

Standard deviations in parentheses.
We used $b_O = 5{\cdot}80 \times 10^{-12}$ and $b_S = 2{\cdot}847 \times 10^{-12}$ mm.

b_{Ho}	Occupation of Ho (2*d*)	Occupation of O (2*d*)	Occupation of S (1*a*)	u_{Ho}	v_O	B_{Ho} (Å²)	B_O (Å²)	B_S (Å²)	R_B (%)	R_{pr} (%)
8·45 (25)	1·0*	1·0*	1·0*	0·2812 (5)	0·6297 (6)	0·40 (10)	0·24 (20)	0·28 (24)	4·13	11·16
8·16 (17)	1·0*	1·0*	1·049 (33)	0·2813 (5)	0·6298 (6)	0·25*	0·55*	0·76 (31)	3·81	11·09

* These parameters were not refined.

Grenoble. With a wavelength of 1·11 Å we recorded 73 Bragg reflexions between $2\theta = 11$ and $2\theta = 56{\cdot}5°$. The refinement was also carried out by the profile analysis method and the results are reported in Table 1. We notice that the correlations between b_{Ho} and B_O are still high. Therefore, for $T = 4{\cdot}2$ K, we report also the curve of b_{Ho} as a function of B_O (Fig. 1).

The study of Ho_2O_3 powders shows that the structural parameters can be well determined: they are in good agreement for example with those obtained in Y_2O_3 (Bonnet, Delapalme & Fuess, 1975). Nevertheless, it is difficult to obtain an accurate value for the scattering length of holmium. Indeed, the refinements show the existence of strong correlations between the holmium scattering length and the thermal parameter of oxygen B_O due to the structure of Ho_2O_3. However, from the two measurements it is possible to show that the published scattering length of holmium, $b_{Ho} = 8{\cdot}5 \times 10^{-12}$ mm, is too high. For satisfactory vibrational parameters of oxygen, the value of b_{Ho} we obtain is in the range $8{\cdot}0 \times 10^{-12}$ to $8{\cdot}4 \times 10^{-12}$ mm.

Determination from powder Ho_2O_2S

The correlation between b_{Ho} and B_O originates from the structure of the cubic oxide Ho_2O_3. As we have already obtained a good result for the structural study of Nd_2O_3 (Boucherle & Schweizer, 1975) which crystallizes in the *A* form of the sesquioxide, we examined another compound containing holmium and oxygen with this type of structure: holmium oxysulphide, Ho_2O_2S. This compound crystallizes in space group *P*3*m* with one formula unit in the unit cell. The atoms occupy the following positions (Zachariasen, 1949):

$$\begin{array}{lll} \text{Ho} & (2d) \pm & (\tfrac{1}{3},\tfrac{2}{3},u), \\ \text{O} & (2d) \pm & (\tfrac{1}{3},\tfrac{2}{3},v), \\ \text{S} & (1a) & (0,0,0). \end{array}$$

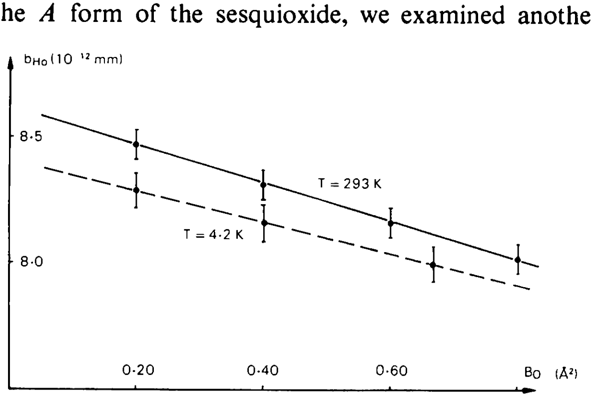

Fig. 1. Variation of the holmium scattering length b_{Ho} as a function of the oxygen temperature factor B_O.

The powder was synthesized from Ho_2O_3 in a H_2S flowing-atmosphere furnace at a temperature between 1273 and 1373 K over 12 h (Picon & Patrie, 1956).

A powder pattern was recorded on the multidetector D1B at the ILL high-flux reactor at Grenoble. The wavelength was 1·22 Å. Data were registered between $2\theta = 6{\cdot}00$ and $2\theta = 85{\cdot}90°$ corresponding to 68 Bragg reflexions. This pattern was analysed by a profile method. Refined parameters are reported in Table 2.

In a first refinement, the composition was supposed to be stoichiometric. But in these compounds the composition is not well defined; the oxygen and rare-earth atoms form sheets with rigid arrangements of tetrahedra, so the stoichiometry between oxygen and holmium is well determined. But the interstitial sulphur site (1*a*) may be partially occupied by a small amount of oxygen atoms. So in a second refinement the occupancy of the 1(*a*) site was determined. On the other hand, the refined thermal parameters are doubtful because of high correlations, so in the second refinement the values for the holmium and oxygen atoms were fixed at those obtained in the isomorphous compound Nd_2O_3 (Boucherle & Schweizer, 1975) where the correlations are lower; we obtained $b_{Ho} = 8{\cdot}16\,(17) \times 10^{-12}$ mm.

Determination from $HoAl_2$ single crystal using polarized neutrons

Because of uncertainties due to correlations with the thermal parameters, which appear in the b_{Ho} determination in Ho_2O_3 as well as in Ho_2O_2S, it is more accurate to measure b_{Ho} directly on a $HoAl_2$ single crystal, taking advantage of polarized neutron sensitivity. Usually, polarized neutrons are used to determine magnetic amplitudes when the nuclear ones are known. Here we used them in the opposite way, determining small nuclear amplitudes knowing the magnetic ones.

In the Laves phases of $MgCu_2$-type structures (Wernick & Geller, 1960), the reflexions (type *e*) corresponding to $h,k,l = 4n$ and $h + k + l = 8n + 4$ have the following nuclear structure factor:

$$F_N = -8\,[b_{\rm Ho} \exp(-B_{\rm Ho} \sin^2\theta/\lambda^2) - 2b_{\rm Al} \exp(-B_{\rm Al} \sin^2\theta/\lambda^2)]. \quad (1)$$

This structure factor is particularly small for reflexions 400 and 444. Therefore an accurate knowledge of F_N leads for these reflexions to a very precise determination of $b_{\rm Ho}$ by comparison with the precise value $b_{\rm Al}$, with the condition that $B_{\rm Ho}$ and $B_{\rm Al}$ are already determined. So a refinement of the thermal parameters was carried out with two sets of data: the flipping ratios,

$$R = (F_N + F_M)^2/(F_N - F_M)^2,$$

determined for each reflexion on a polarized neutron diffractometer and the integrated intensities of these reflexions recorded with unpolarized neutrons. These intensities include both nuclear and magnetic contributions; $I = F_N^2 + F_M^2$. They are deconvoluted by the ratios $\gamma = F_M/F_N$ deduced from the flipping ratios R;

$$F_N^2 = I/(1 + \gamma^2).$$

Experiments were performed at 4·2 K (Boucherle, 1977). The same crystal, a platelet of 0·7 mm thickness, was used for both measurements. For 17 different Bragg reflexions, the integrated intensities (at $\lambda = 0{\cdot}71$ Å) and the flipping ratios were measured. The comparison of the flipping ratios of the same reflexion at different wavelengths provides a very good determination of the extinction parameters (Bonnet, Delapalme, Becker & Fuess, 1976). From 42 flipping ratios measured at three different wavelengths (0·84, 0·50, 0·42 Å), we obtained the parameters of the mosaïc crystal theory (Zachariasen, 1967; Becker & Coppens, 1975): $t = 11{\cdot}5\,(1{\cdot}1)$ µm for the size of mosaic blocks and $\eta = 1{\cdot}81\,(25)'$ for the mosaic spread.

From the experimental F_N^2 values, a refinement gives the scale factor and the thermal parameters of the two atoms:

$$B_{\rm Ho} = 0{\cdot}17\,(3)\ \text{Å}^2, \quad B_{\rm Al} = 0{\cdot}42\,(6)\ \text{Å}^2.$$

Then, for the two reflexions 400 and 444, whose nuclear structure factor is very small, one determines very accurately their value from the γ ratio on one hand and from the integrated intensity (whose absolute value is calculated with the previously determined scale factor) on the other. Using the value $b_{\rm Al} = 3{\cdot}449\,(9) \times 10^{-12}$ mm, one deduces from (1) a value of $b_{\rm Ho}$ for each of the two reflexions. They are reported in Table 3 together with the experimental values of I, F_N, F_M and γ. The values found for $b_{\rm Ho}$ agree. They agree also with a third value which was refined together with $B_{\rm Ho}$ and $B_{\rm Al}$ from the 17 values of F_N^2, namely $b_{\rm Ho} = 8{\cdot}05\,(9) \times 10^{-12}$ mm. So the final value determined in $HoAl_2$ is:

$$b_{\rm Ho} = 8{\cdot}08\,(5) \times 10^{-12}\ \text{mm}.$$

Table 3. *Integrated intensities, γ values, magnetic and nuclear structure factors and $b_{\rm Ho}$ (in 10^{-12} mm) measured or determined for* $HoAl_2$ *reflexions of type e*

hkl	*I*	γ	F_M	F_N	$b_{\rm Ho}$
400	220·8 (7·4)	14·18 (40)	14·82 (25)	1·04 (4)	8·10 (6)
444	95·7 (3·2)	8·25 (31)	9·71 (16)	1·18 (10)	8·07 (10)

Conclusion

This study shows the limitation of the scattering length determination by precise neutron diffraction measurements on powders and comparison with standards which are here oxygen and sulphur. Correlations between scattering length and temperature factors reduce in a noticeable way the accuracy of the result. This was particularly true in the case of cubic Ho_2O_3. For trigonal Ho_2O_2S, the use of temperature factors for the rare earth and oxygen atoms determined in isomorphous Nd_2O_3, in which correlations are lower, allowed a reduction of this effect.

These limitations underline the interest in the determination of scattering lengths with single crystals of simple structure such as RAl_2, as has already been done for neodymium (Boucherle & Schweizer, 1975), by means of both polarized and unpolarized neutrons.

The value found for holmium:

$$b_{\rm Ho} = 8{\cdot}08\,(5) \times 10^{-12}\ \text{mm},$$

is quite different from the published value, but is consistent with the results obtained for the compounds Ho_2O_3 and Ho_2O_2S.

References

Becker, P. & Coppens, P. (1975). *Acta Cryst.* A**31**, 417–425.

Bonnet, M., Delapalme, A., Becker, P. & Fuess, H. (1976). *Acta Cryst.* A**32**, 945–953.

Bonnet, M., Delapalme, A. & Fuess, H. (1975). *Acta Cryst.* A**31**, 264–265.

Boucherle, J. X. (1977). Thesis. Univ. Grenoble.

Boucherle, J. X. & Schweizer, J. (1975). *Acta Cryst.* B**31**, 2745–2746.

Convert, P. (1975). Thesis. Univ. Grenoble.

Hewat, A. W. (1973). *J. Phys. C*, **6**, 2559–2572.

Koehler, W. C., Wollan, E. O. & Wilkinson, M. K. (1958). *Phys. Rev.* **110**, 37–40.

Picon, M. & Patrie, M. (1956). *C. R. Acad. Sci.* **242**, 516–518.

Rietveld, H. M. (1967). *Acta Cryst.* **22**, 151–152.

Rietveld, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.

Wernick, J. H. & Geller, S. (1960). *Trans Metall. Soc. AIME*, **218**, 866.

Zachariasen, W. H. (1949). *Acta Cryst.* **2**, 60–62.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.