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A Neutron-Diffraction Study of the Tetragonal Crystal Structures of Some Yttrium–Holmium Dicarbides

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Crystal structure line profile refinements have been made for neutron powder diffraction data collected at room temperature from the ternary yttrium–holmium dicarbides $Y_xHo_{1-x}C_2$, with $x = 0.75$, 0.50, and 0.25, and the binary dicarbides YC_2 and HoC_2. The five compounds are isostructural, with tetragonal unit-cell dimensions in the range $a = 3.663(1)$, $c = 6.171(1)$ Å (for YC_2) to $a = 3.646(1)$, $c = 6.142(1)$ Å (for HoC_2), and they contain discrete acetylenic C–C groups with carbon–carbon bond lengths close to 1.28 Å.

1. Introduction

The technological importance of the transition-metal carbides, arising from novel high temperature (*1*), mechanical, and electrical properties, has for a long time stimulated interest (*2*) in the structure, bonding, and phase transitions in carbides covering a wide composition range. For carbides in which the carbon/metal ratio exceeds unity, a combination of chemical, X-ray, and neutron diffraction evidence points to the presence of dimeric C_2^{2-} structural units (*3–8*), which are responsible for diffusionless phase transformations, usually from a low temperature tetragonal form to a high temperature cubic modification (*9, 10*). Within the C_2 units of binary dicarbides, the C–C distance tends to increase with cationic charge: 1.20, 1.27, and 1.34 Å, respectively, in CaC_2, LaC_2, and UC_2 (*6*), and might be expected to increase as the proportions of higher atomic number lanthanide in ternary carbides increase (owing to greater electron concentration in the metal $(4f - 5d)C_22p\pi^*$ bond).

For the carbides of the heavier metals, particularly if disorder is suspected, neutron diffraction is greatly preferable to X-ray diffraction for unambiguous location of carbon atom positions in the crystal structures and so for distinguishing between C_2^{2-} dimer models for structural transitions. Moreover, where sufficiently large single crystals cannot be produced, refinement of the detailed shape or profile (*11, 12*) of the diffraction pattern provides an effective means whereby low atomic number atom positions may be derived from neutron powder diffraction data, even if few individual diffraction lines are well resolved. As part of a study of carbon–carbon distances and orientations in reactive hybrid carbides $M_xM'_{1-x}C_2$, where M and M' are

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combinations of 3*d*, 4*f*, or 5*f* metals (*13*, *14*), we report here a room-temperature neutron diffraction study of the crystal structures of the dicarbides of yttrium and holmium, $Y_xHo_{1-x}C_2$ over the range x = 0–1. This appears to be the first example of the anisotropic profile refinement of neutron data in the determination of dicarbide structures.

2. Experimental

2.1. Sample preparation. The carbides were prepared by direct high temperature synthesis from stoichiometric quantities of the constituent elements in an argon arc furnace. The lanthanide metals (>99.9%, Rare-Earth Products Limited) and the Specpure graphite rods were in the form of coarse grains or lumps (rather than powder) in order to eliminate losses due to removal of finely divided powder from the reaction zone by the pressure of the arc flame (*3*, *4*, *9*). The presence of about 3% excess graphite ensured removal of any oxide in the metals. Phase purity was checked by optical microscopy and X-ray powder photographs and by absence of lines due to graphite on the neutron-diffraction powder patterns.

Each preparative run yielded a 0.5–1.0 g pellet of carbide; this was pulverized in a percussion mortar in a dry-argon atmosphere. The products of about 10 preparative runs were then combined to give about 0.01 mole of material for use in the neutron diffraction measurements. In this way, three yttrium–holmium dicarbides, $Y_xHo_{1-x}C_2$ (x = 0.75, 0.50, 0.25), and two binary dicarbides, YC_2 and HoC_2, were prepared.

2.2. Collection of neutron diffraction data. Neutron diffraction patterns of the samples, contained in a thin-walled 5-mm-diameter cylindrical vanadium can, were recorded at room temperature on the D2 diffractometer at the High Flux Reactor of the Institut Laue-Langevin, Grenoble, with slit angles α_1 = 30 min, α_2 = 30 min, and α_3 = 20 min. The neutron wavelength (determined from a powder diffraction pattern on annealed nickel powder) was λ = 1.119 Å, and the step increment was 0.1° (2θ) with 2θ ranging from 10 to between 100 and 120°. With a counting time of about 40 sec per point, the complete diffraction pattern was obtained within 10 to 12 hr. The diffraction patterns for all five dicarbides were qualitatively similar and taken to have the calcium dicarbide structure. The background attributed to paramagnetic scattering, appreciable for HoC_2, decreased progressively as x increased. The absence of superlattice lines in the ternary compounds was interpreted as indicating random occupation of the metal sites (at 0, 0, 0) by the two metal species in these structures.

2.3. Structure refinement. The starting point for the refinement of all five crystal structures was essentially the body-centered tetragonal unit cell *I4/mmm* (described by Atoji (*17*) as a tetragonally deformed NaCl-type packing of rare-earth atoms and C_2 molecules). This structure was established by Spedding *et al.* (*15*) by powder X-ray diffraction for HoC_2 and YC_2 and confirmed for the same compounds by Atoji (*16*, *17*) by refinement of neutron diffraction peak intensities. The present profile refinement (carried out with a modified version (*12*) of the Rietveld program) involved least-square minimization of a quantity

$$\chi^2 = \Sigma w_i |y_i(\text{obs}) - \frac{1}{c} y_i(\text{calc})|^2 \qquad (1)$$

where y_i(obs) and y_i(calc) are the observed and calculated counts at each 2θ point i in the diffraction pattern, and w_i is the weighting factor. The χ^2 was minimized with respect to the following crystal-structural and instrumental parameters (13 in all):

(1) The tetragonal (*I4/mmm*) unit-cell parameters a and c.

(2) The anisotropic temperature parameters B_{ij} for the metal and carbon atoms, subject to the constraints (*18*) $B_{11} = B_{22}$ and $B_{12} = B_{13} = B_{23} = 0$.

(3) The z-parameter of the carbon atom (carbon atoms are located at 0, 0, $\pm z$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \pm z$).

(4) An overall scale factor, c.

(5) The three parameters U, V, and W in

$$H^2 = U \tan^2 \theta + V \tan \theta + W \quad (2)$$

(where H is the full width at half-height of the Gaussian curve for the reflection at Bragg angle θ).

(6) A counter zero-point parameter, Z (*11*).

(7) A peak-asymmetry parameter, P (*11*).

Initial values for these parameters:

(1) Unit-cell parameters for YC_2 and HoC_2 were taken from Spedding *et al.* (*15*), with linearly interpolated values for the mixed yttrium/holmium compositions.

(2) $B_{11} = B_{33} = 0.5$ Å^2 for both metal and carbon atoms.

(3) From Atoji for YC_2 (*16*) and HoC_2 (*17*), and by interpolation for the mixed yttrium/holmium compositions.

(4) In several preliminary cycles of refinement, only the scale factor and unit-cell parameters were varied in order to derive an initial value for the scale factor.

(5) U, V, and W were determined from a least-square fit to Eq. (2) of the measured half-height widths of seven reflections in the diffraction pattern of annealed nickel powder (all the reflections in the face-centered cubic pattern were used up to 422, except 331 and 420 which were incompletely resolved).

(6,7) Z and P were both set initially to zero. The neutron scattering amplitudes used were $b_Y = 7.65$ fm (*19*); $b_{Ho} = 8.08$ fm (*20*), $b_C = 6.65$ fm (*21*); in the mixed yttrium/holmium compositions, the effective metal-atom scattering amplitudes were the appropriately weighted means of those for yttrium and holmium.

In general, the least-square minimizations partially converged after four or five cycles, but some oscillation of thermal parameters persisted. This tendency was overcome by applying only a fraction of the calculated shift to all the temperature parameters in each cycle, and by extending the refinement to about 12 cycles. Thus for $Y_{0.5}Ho_{0.5}C_2$, for which the temperature parameters B_{11} for the metal site and B_{33} for the carbon atom tended to go nonpositive definite, shifts of only one-tenth of those predicted were applied. Similarly, for HoC_2, oscillating shifts for some of the temperature parameters were overcome by applying only one-half of the calculated shifts for several cycles before convergence was achieved. In the final cycle of all five refinements, the shift in any parameter did not exceed one-half of the estimated standard deviation (e.s.d.) and in most cases was less than 0.05 times the e.s.d. The final agreement factors (Table I) are

$$R = \sum_i \{|y_i(\text{obs}) - \frac{1}{c}\, y_i(\text{calc})|\}/\Sigma|y_i(\text{obs})| \quad (3)$$

$$R_w = \sqrt{[\Sigma w_i\{y_i(\text{obs}) - \frac{1}{c}\, y_i(\text{calc})\}^2/\Sigma w_i\{y_i(\text{obs})\}^2]} \quad (4)$$

Figure 1 illustrates the observed, calculated, and discrepancy profiles for $Y_{0.25}Ho_{0.75}C_2$; lists of observed and calculated intensities for all points in the five compounds have been deposited.[1] Correla-

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[1] See NAPS document No. 04186 for 5 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material. Remit $1.50 for postage of any microfiche orders.

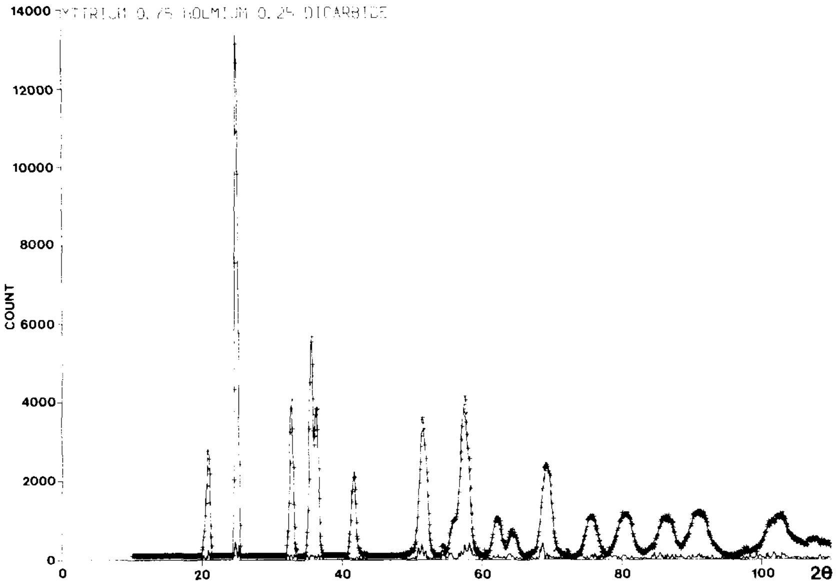

FIG. 1. Neutron powder diffraction diagram for $Y_{0.75}H_{0.25}C_2$: solid line, calculated profile; crosses, experimental intensities; differences between these are shown at the bottom.

tion matrices from the final cycles of refinement indicated some strong correlations between shifts for parameters within the following groups.

(1) The anisotropic temperature parameters (correlation coefficients up to 0.7); (2) The parameters U, V, and W (correlation coefficients greater than 0.9); and (3) The unit-cell parameters, the zero-point parameter and the asymmetry parameter (correlation coefficients 0.4 to 0.9).

While there were no significant correlations between shifts for parameters in different groups, shifts in the scale factor were significantly correlated (coefficients 0.2 to 0.3) with those in some of the temperature parameters, particularly B_{33} for the metal atom and B_{11} for the carbon atom. The z-parameter of the carbon atom was not significantly correlated with any other parameter (maximum correlation coefficient = 0.12).

Application of absorption corrections (coefficients in Table I calculated from mass absorption coefficients Y, 0.006; Ho, 0.115; C, 0.00015 cm^2 g^{-1}) in accordance with the Hewat procedure (*23*) produces corrections, ΔB, to the temperature factors (Table I) which are smaller than the apparent e.s.d.'s.

3. Results and Discussion

The final refined structural parameters for the five dicarbides are shown in Table I. No thermal vibration corrections were applied to the apparent C–C bond lengths since none of the usual models (*22*) seemed appropriate: the effect of such a correction would be to lengthen the distance slightly.

The unit-cell dimensions decrease progressively with increasing holmium content; for c, the change is marginally smaller from YC_2 to $Y_{0.75}Ho_{0.25}C_2$ than elsewhere. For YC_2 and HoC_2, the cell dimensions do not differ significantly from those reported from room-temperature X-ray measurements (*15*); at higher temperatures, the YC_2 cell is, of course, larger (a = 3.74, c = 6.20

TABLE I

RESULTS OF NEUTRON POWDER PROFILE REFINEMENTS FOR FIVE $Y_xHo_{1-x}C_2$ COMPOUNDS

x	1	0.75	0.50	0.25	0
a	3.663(1)	3.660(1)	3.657(1)	3.651(1)	3.646(1)
c	6.171(1)	6.166(1)	6.158(1)	6.149(1)	6.142(1)
z_C	0.3957(3)	0.3959(2)	0.3959(2)	0.3959(2)	0.3954(2)
B_{11}(M)	0.23(9)	0.30(6)	0.22(6)	0.26(5)	0.34(6)
B_{33}(M)	0.81(17)	1.03(14)	1.01(14)	0.83(10)	0.80(13)
B_{11}(C)	0.35(6)	0.71(6)	0.69(6)	0.72(5)	0.64(6)
B_{33}(C)	0.27(11)	0.38(9)	0.25(9)	0.54(8)	0.56(10)
μ	0.02	0.27	0.51	0.76	1.01
ΔB	<0.001	<0.01	0.014	0.03	0.04
R	0.103	0.085	0.086	0.080	0.103
R_w	0.115	0.093	0.092	0.085	0.103
C–C	1.288(3)	1.284(3)	1.282(3)	1.281(3)	1.285(3)

Note. Unit cell dimensions, a and c (Å), fractional z-coordinates of carbon, z_C, temperature factors, $B_{jj} = 8\pi^2 U_{jj}$ (Å^2), absorption coefficients (in μ/cm^{-1}), absorption corrections to B, ΔB, unweighted (R), and weighted (R_w) agreement factors, and C–C bond lengths (Å) (e.s.d.'s of least significant figures in parentheses).

Å from neutron diffraction at 1100° (*24*)). Within the accuracy of our determination, the C–C bond lengths are the same for all five materials (although the actual values are lower in the $x = 0.25$–0.50 composition range). The C–C distance of 1.288(3) Å in YC_2 is significantly larger than that of 1.275(2) Å reported by Atoji (*16*); however, the C–C length of 1.285(3) Å obtained for HoC_2 does not differ significantly from Atoji's (*17*) value of 1.279 Å.

Of the anisotropic temperature factors, B_{33} for the metal atoms is consistently larger than B_{11}; for the carbon atoms, B_{11} tends to be larger than B_{33}, i.e., thermal vibration is greater perpendicular to C–C (along a) than parallel to C–C (along the c-axis). However, the carbon B_{11} for YC_2 seems to be anomalously low. The negligible carbon B_{33} values for carbides containing 50% or more of yttrium may be associated with stronger C–C bonds in the materials; this would be consistent with the presence of strong metal–metal bonds between yttrium atoms, with consequent weakening of the metal-carbon bonds.

Finally, we note that the refined half-height width parameters do not differ significantly from the starting values (as obtained from the nickel diffraction pattern) for any of the five analyses; typical values are $U = 8.2$, $V = -3.1$, and $W = 0.54$. The refined values of the zero-point and asymmetry parameters ($Z = 0.03°$ and $P = 2 \times 10^{-5}$ for $Y_{0.5}Ho_{0.5}C_2$) from the five analyses are all essentially the same.

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