*Acta Cryst.* (1962). **15**, 252

# The Structures of $NiZr_2$, NiZr and their Hafnium Analogs*

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(*Received* 7 *September* 1960 *and in revised form* 8 *December* 1960)

The crystal structures of the intermediate phases $NiZr_2$ and NiZr were determined by single crystal methods. The structure of the tetragonal $NiZr_2$ phase was found to be the C16 type with space group symmetry $D_{4h}^{18}$-$I4/mcm$. The lattice dimensions for this phase were found to be $a_0=6{\cdot}477$ and $c_0=5{\cdot}241$ Å. Lattice dimensions for the orthorhombic NiZr lattice were found to be

$$a_0=3{\cdot}268,\ b_0=9{\cdot}937,\ c_0=4{\cdot}101\ \text{Å}\ .$$

The structure of NiZr was established as the $B_f$ structure with $D_{2h}^{17}$-$Cmcm$ space group symmetry. Sufficient data on $NiHf_2$ and NiHf were taken to verify that these compounds are isostructural with their corresponding zirconium compounds.

## Introduction

The crystal structures of the intermediate phases $NiZr_2$, $NiHf_2$, NiZr, and NiHf have been determined by single crystal methods and the structure details are presented in this paper. The existence of the two intermediate phases, $NiZr_2$ and NiZr, was first reported by Hayes, Roberson & Paasche (1953); however, they were unable to identify the structures of either of these phases from polycrystalline diffraction data. Libowitz, Hayes & Gibb (1958) studied the system NiZr–H and found that the phases NiZr, NiZrH and $NiZrH_3$ gave similar diffraction patterns which were tentatively indexed on the basis of a distorted cubic cell with lattice parameter varying between 6·98 Å and 7·40 Å. The results of the present investigation do not corroborate the tentative indexing, but rather indicate that the phase NiZr has the orthorhombic $B_f$ type structure (*Structure Reports*, **12**, p. 30, 1949) typified by ζ-CrB as reported by Kiessling (1949).

The phase relationships for the zirconium-rich portion of the nickel–zirconium system were found by Kirkpatrick (1958) to be similar to those reported by Hayes *et al.* (1953). On the basis of these phase relationships, single crystal specimens of the nickel–zirconium phases were prepared by heating alloys of zirconium-rich composition, with respect to stoichiometry, to just above the eutectic isotherm and allowing gravitational separation of the liquid phase from the rigid network of primary crystals. Thus, all nickel–zirconium crystals used in this investigation have compositions which are essentially those of the zirconium-rich phase boundaries. The compositions of the hafnium–nickel crystals used in the investigation are also those of the hafnium-rich phase boundaries.

The procedures and data common to the structure determinations herein reported are noted at this point to avoid repetition. The refinement of trial structures was carried out using the least squares program for the IBM-650 of Senko & Templeton as modified by Fitzwater (1958). The atomic form factors were those of Thomas & Umeda (1957) corrected for dispersion effects in the manner of Dauben & Templeton (1955). Absorption corrections were made in the manner of Bradley (1935) with the approximation of cylindrical geometry for the needle-shaped crystals. All intensity data were corrected for Lorentz and polarization effects. The Fourier projections were prepared with the computer program of Fitzwater & Williams (1958).

## Structure determination of $NiZr_2$

Diffraction symmetry and characteristic extinctions for $NiZr_2$ were obtained from *hk*0 and *hk*1 Weissenberg data and *hhl*, *h*0*l*, and *h*1*l* precession data. These data indicated tetragonal symmetry with the probable space group $D_{4h}^{18}$-$I4/mcm$, $C_{4v}^{10}$-$I4cm$, or $D_{2d}^{10}$-$I\bar{4}c2$. Lattice parameters $a_0=6{\cdot}477\pm0{\cdot}004$ and $c_0=5{\cdot}241\pm0{\cdot}006$ Å were obtained by extrapolation, respectively, against the Nelson–Riley (1945) function for Weissenberg data and against $\cos^2\theta$ for rotation data. The precision parameters were combined with the density to compute a unit cell content of four formula weights. This cell content gives a theoretical density which equals the experimental value of 7·28 g.cm.$^{-3}$.

Visually estimated *h*0*l* intensity data were obtained from timed exposures taken with Mo $K\alpha$ radiation on a precession camera. A Patterson projection, $P(x, z)$, was prepared with these intensity data. Since adjustable $z$-parameters were not indicated by this projection, space group $C_{4v}^{10}$-$I4cm$ was dropped from consideration. Further, the allowed atomic positions in $D_{2d}^{10}$-$I\bar{4}c2$ differ from those in $D_{4h}^{18}$-$I4/mcm$ by a single eight-fold set which is incompatible with the Patterson

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* Contribution No. 943. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

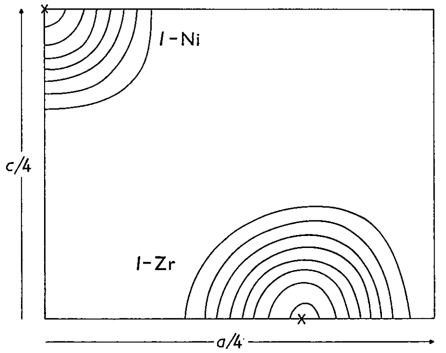

Fig. 1. Electron density projection, $\varrho(x, z)$, for the phase $NiZr_2$. Each maximum represents a single atom.

projection. Thus, space group $D_{4h}^{18}$–$I4/mcm$ was chosen and the following trial structure was postulated:

$$\text{Space group } D_{4h}^{18}\text{–}I4/mcm$$

with

$$4\,\text{Ni} \quad \text{at} \quad (0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}) + (0, 0, \tfrac{1}{4};\ 0, 0, \tfrac{3}{4})$$

and

$$8\,\text{Zr} \quad \text{at} \quad (0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}) \pm (x, \tfrac{1}{2}+x, 0;\ \tfrac{1}{2}+x, \bar{x}, 0)$$

with

$$x = 0{\cdot}167\ .$$

The refinement of the trial structure produced values for

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0{\cdot}0757$$

and

$$R_2 = \Sigma(|F_o| - |F_c|)^2/\Sigma F_o^2 = 0{\cdot}0084$$

with $x = 0{\cdot}1629 \pm 0{\cdot}0025$, $B_{\text{Zr}}/\lambda^2 = 2{\cdot}327$ and $B_{\text{Ni}}/\lambda^2 = 1{\cdot}835$. The refined structure is the $C16$ structure (*Strukturbericht*, **1**, p. 491, 1913–1928) typified by $CuAl_2$ as reported by Friauf (1927). Interatomic distances for this structure were computed with the distance program for the IBM-650 computer and are given in Table 1. The observed and calculated structure factors are compared in Table 2. A Fourier projection, $\varrho(x, z)$, based on the final structure parameters is shown in Fig. 1.

Table 1. *Interatomic distances in* $NiZr_2$

| Atom | Neighbor | Number of neighbors | Distance |
|---|---|---|---|
| Ni | Ni | 2 | 2·62 Å |
| | Zr | 8 | 2·76 |
| Zr | Ni | 4 | 2·76 |
| | Zr | 1 | 2·98 |
| | Zr | 2 | 3·07 |
| | Zr | 4 | 3·36 |
| | Zr | 4 | 3·43 |

Table 2. *Observed and calculated structure factors for* $NiZr_2$

| $h0l$ | $\|F_o\|$ | $F_c$ | $h0l$ | $\|F_o\|$ | $F_c$ |
|---|---|---|---|---|---|
| 002 | 34·0 | +35·1 | 402 | 37·2 | −37·4 |
| 004 | 51·0 | +51·1 | 404 | < 3·0 | − 4·8 |
| 006 | 13·5 | +12·7 | 406 | 18·9 | −18·3 |
| 200 | < 1·9 | − 4·8 | 600 | 41·4 | +41·7 |
| 202 | 48·4 | −42·6 | 602 | 16·9 | +15·9 |
| 204 | < 2·8 | − 2·1 | 604 | 27·4 | +29·3 |
| 206 | 16·8 | −18·5 | 800 | 3·2 | + 2·2 |
| 400 | 8·4 | − 8·4 | 802 | 11·6 | −13·9 |

## Structure determination of NiZr

For the purpose of symmetry determination, $0kl$ and $1kl$ Weissenberg and $hk0$, $hk1$, $h0l$, and $hll$ precession photographs were obtained. The diffraction symmetry and characteristic extinctions indicated orthorhombic space group $D_{2h}^{17}$–$Cmcm$, $C_{2v}^{16}$–$C2cm$ or $C_{2v}^{12}$–$Cmc2_1$. The lattice dimension $a_0 = 3{\cdot}268 \mp 0{\cdot}008$ Å was obtained from extrapolation of rotation data. The dimensions $b_0 = 9{\cdot}937 \mp 0{\cdot}004$ Å and $c_0 = 4{\cdot}101 \mp 0{\cdot}005$ Å were obtained by extrapolation of Weissenberg data in the manner of Nelson & Riley (1945). A theoretical density of $7{\cdot}47 \mp 0{\cdot}03$ g.cm.$^{-3}$ for the structure can be computed if it is assumed that there are four formula weights of NiZr per cell. This theoretical density is in good agreement with the observed density of 7·43 g.cm.$^{-3}$ which was measured on a massive alloy of stoichiometric composition.

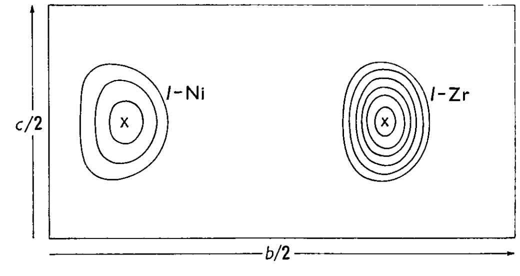

Fig. 2. Electron density projection, $\varrho(y, z)$, for the phase NiZr. Each maximum represents a single atom.

Visually estimated $0kl$ and $1kl$ intensity data were obtained from multiple film Weissenberg photographs taken with Cu $K\alpha$ radiation. In addition, visually estimated $hk0$ data were obtained from timed exposures taken on the precession camera with Mo $K\alpha$ radiation. The Patterson projection, $P(y, z)$, plus the apparently normal intensity decline in $h00$ and $00l$ reflections were used to postulate the following trial structure:

$$\text{Space group } D_{2h}^{17}\text{–}Cmcm$$

with

$$4\,\text{Ni} \quad \text{at} \quad (0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, 0) \pm (0, y_1, \tfrac{1}{4}),\ y_1 = 0{\cdot}10$$

and

$$4\,\text{Zr} \quad \text{at} \quad (0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, 0) \pm (0, y_2, \tfrac{1}{4}),\ y_2 = 0{\cdot}35\ .$$

During the refinement, an attempt was made to verify the choice of the centric space group $D_{2h}^{17}$–$Cmcm$ by the introduction of adjustable $x$ and $z$ parameters. Displacement of the $x$ parameter from the centric values of the trial structure creates the symmetry of space group $C_{2v}^{16}$–$C2cm$, whereas displacement of the $z$ parameters creates the symmetry of space group $C_{2v}^{12}$–$Cmc2_1$. Trial structures were chosen in space group $C_{2v}^{16}$ with values for $x$ shifted in the various possible combinations from the centric values of $X_1 = X_2 = 0$ for the two fourfold sets and in space group $C_{2v}^{12}$ with values for $z$ also shifted in the various possible combinations from the centric values of $Z_1 = Z_2 = \frac{1}{4}$. Refinement in all cases led to the centric values for the $x$ and $z$ coordinates, thus substantiating the choice of space group $D_{2h}^{17}$–$Cmcm$. The centric refinement of $0kl$ and $1kl$ data produced values for

$$R_1 = 0{\cdot}1302 \quad \text{and} \quad R_2 = 0{\cdot}0274$$

with

$$y_1 = 0{\cdot}0817 \pm 0{\cdot}0017,\ y_2 = 0{\cdot}3609 \pm 0{\cdot}0008\ ,$$
$$B_{\mathrm{Ni}}/\lambda^2 = 0{\cdot}670 \quad \text{and} \quad B_{\mathrm{Zr}}/\lambda^2 = 0{\cdot}242\ .$$

Refinement of $hk0$ data resulted in a model having the above positional parameters and values for $R_1 = 0{\cdot}1276$ and $R_2 = 0{\cdot}0181$ with $B_{\mathrm{Ni}}/\lambda^2 = 0{\cdot}890$ and $B_{\mathrm{Zr}}/\lambda^2 = 2{\cdot}829$. Since no explicit absorption corrections were made for the $hk0$ intensity data, the differences between temperature factors are presumably due to differences in the absorption effects of Mo $K\alpha$ and Cu $K\alpha$ radiation. The refined structure is the $B_f$ structure typified by ζ-CrB. Interatomic distances for the NiZr structure are listed in Table 3. The observed and calculated structure factors are compared in Table 4. A Fourier projection, $P(y, z)$, based on the final structure parameters is shown in Fig. 2.

Table 3. *Interatomic distances in* NiZr

| Atom | Neighbor | Number of neighbors | Distance |
|---|---|---|---|
| Ni | Ni | 2 | 2·62 Å |
| | Ni | 2 | 3·27 |
| | Zr | 4 | 2·68 |
| | Zr | 2 | 2·74 |
| | Zr | 1 | 2·77 |
| Zr | Ni | 4 | 2·68 |
| | Ni | 2 | 2·74 |
| | Ni | 1 | 2·77 |
| | Zr | 2 | 3·27 |
| | Zr | 2 | 3·44 |
| | Zr | 4 | 3·43 |

## The structures $NiHf_2$ and NiHf

Diffraction symmetry and characteristic extinctions for the phases $NiHf_2$ and NiHf were determined from rotation and Weissenberg photographs and were found to be identical with like data from the respective zirconium phases. In addition, qualitative examination of the diffraction intensities of Weissenberg and Debye–Scherrer photographs shows a close correlation in relative intensities between corresponding reflections of the analogous hafnium and zirconium phases. This evidence is considered to be adequate to verify that $NiHf_2$ and NiHf are isostructural with $NiZr_2$ and NiZr, respectively.

Lattice dimensions for the phase $NiHf_2$ were found to be $a_0 = 6{\cdot}743 \mp 0{\cdot}006$ Å and $c_0 = 5{\cdot}58 \mp 0{\cdot}01$ Å. These dimensions are slightly larger than would be expected on the basis of data from $NiZr_2$ with due consideration of the close correspondence in atomic size of hafnium and zirconium. This difference in cell volume may be due to either greater solubility of hafnium in $NiHf_2$

Table 4. *Observed and calculated structure factors for* NiZr

| $0kl$ | $\|F_o\|$ | $F_c$ | $1kl$ | $\|F_o\|$ | $F_c$ | $hk0$ | $\|F_o\|$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|
| 020 | 18·4 | +12·7 | 110 | 9·8 | −10·2 | 200 | 106·8 | +101·3 |
| 021 | 46·9 | +38·9 | 130 | 54·6 | +65·0 | 400 | 44·4 | +49·9 |
| 022 | 12·3 | − 6·5 | 150 | 13·7 | − 6·2 | 110 | 6·6 | − 2·4 |
| 023 | 32·3 | −31·5 | 170 | 67·6 | −75·3 | 310 | 10·1 | + 2·5 |
| 024 | < 4·6 | + 1·1 | 190 | < 6·4 | − 1·3 | 220 | 12·3 | +11·4 |
| 040 | 87·2 | −90·5 | 1,11,0 | 50·3 | +47·4 | 420 | 9·3 | + 7·7 |
| 041 | 67·4 | −59·1 | 111 | 69·8 | −78·6 | 130 | 60·5 | +64·0 |
| 042 | 70·4 | +71·3 | 112 | 12·2 | +12·1 | 330 | 30·6 | +33·2 |
| 043 | 40·3 | +36·2 | 113 | 53·6 | +51·4 | 040 | 102·9 | −93·8 |
| 044 | 50·6 | −45·3 | 114 | 9·9 | −12·7 | 240 | 73·3 | −64·9 |
| 060 | 5·0 | − 1·0 | 131 | 76·4 | −71·9 | 440 | 39·8 | −32·5 |
| 061 | 54·3 | −53·6 | 132 | 55·5 | −52·9 | 150 | 18·9 | −16·5 |
| 062 | < 4·4 | − 2·4 | 133 | 48·1 | +46·0 | 350 | 28·7 | −12·5 |
| 063 | 39·8 | +39·7 | 134 | 44·0 | +35·4 | 060 | 1·3 | − 1·3 |
| 064 | < 3·8 | + 7·4 | 151 | 37·8 | +40·6 | 260 | 9·7 | −11·9 |
| 080 | 28·4 | +26·0 | 152 | 10·4 | + 2·9 | 170 | 72·3 | −80·7 |
| 081 | 52·3 | +50·6 | 153 | 42·2 | −32·3 | 370 | 43·4 | −51·2 |
| 082 | 26·0 | −23·6 | 154 | < 5·1 | + 1·5 | 080 | 10·7 | +14·8 |
| 083 | 48·1 | −37·6 | 171 | 21·3 | +18·7 | 280 | 10·0 | +10·0 |
| 084 | 18·1 | +19·4 | 172 | 63·0 | +63·9 | 390 | 9·3 | − 1·8 |
| 0,10,0 | 30·5 | −26·3 | 173 | 18·6 | −13·4 | 0,10,0 | 16·5 | −15·4 |
| 0,10,1 | 52·6 | +41·2 | 174 | 38·9 | −43·4 | 2,10,0 | 14·5 | −11·2 |
| 0,10,2 | 30·4 | +24·2 | 191 | 31·9 | −26·3 | 1,11,0 | 37·8 | +49·1 |
| 0,10,3 | 33·3 | −31·7 | 192 | < 5·8 | + 1·0 | | | |
| 0,12,0 | 6·2 | − 5·4 | 193 | 23·9 | +23·6 | | | |
| 0,12,1 | 27·9 | −28·8 | 1,11,1 | 19·5 | +14·4 | | | |
| 002 | 84·9 | −107·2 | 1,11,2 | 40·5 | −42·2 | | | |
| 004 | 32·1 | +61·2 | | | | | | |

than zirconium in $NiZr_2$ or to a higher foreign atom content in the $NiHf_2$ crystal examined.

Lattice dimensions of

$$a_0 = 3{\cdot}220 \mp 0{\cdot}005,\ b_0 = 9{\cdot}820 \mp 0{\cdot}006,\ c_0 = 4{\cdot}12 \mp 0{\cdot}01\ \text{Å}$$

were determined from single crystal data for the phase NiHf. It is of interest to note that the dimensions $a_0$ and $b_0$ are somewhat smaller than those for the phase NiZr. However, the $c_0$ dimension is approximately the same for both phases. Since the atomic diameter of hafnium is slightly less than that of zirconium, it is probable that the $c_0$ dimension is controlled by the Ni–Ni contact.

## Discussion

The packing efficiency in both the $C16$ and $B_f$ structures is quite high with an average coordination number of 13 for NiZr and NiHf and of $13\frac{1}{3}$ for $NiZr_2$ and $NiHf_2$. The nickel atoms run through the $NiZr_2$ structure in straight linear chains with an interatomic spacing of 2·62 Å and with all chains parallel one to the other. A similar type of chain array is exhibited in $NiMg_2$ (Schubert & Anderko, 1951) wherein the Ni–Ni bond distance is 2·59 Å, but the linear chain arrangement differs from $NiZr_2$ in that the chains are parallel within a given layer but the orientation rotates 60° from one layer to the next.

A Ni–Ni bond distance of 2·62 Å is also found in NiZr where the closely bonded nickel atoms form wrinkled chains having a Ni–Ni–Ni bond angle of 103° 15′. In this latter case there is also a weaker interaction of each nickel atom with two additional nickels at 3·27 Å.

Only three out of eleven Zr–Zr bonds in $NiZr_2$ and none of the Zr–Zr bonds in NiZr are shorter than the 3·20 Å Zr–Zr bond in elemental zirconium. The Ni–Ni distances in the compounds are longer than the 2·48 Å Ni–Ni bond in elemental nickel. However, all of the Ni–Zr bonds are shorter than 2·84 Å which is the mean of the elemental bond distances. High packing efficiency plus an appreciable Ni–Zr interaction are thus presumed to be responsible for the stability of these compounds.

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# Structural Properties of $(Ba, Pb)_{1-\delta}(Ti, Nb)O_3$ Systems*

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(*Received* 10 *January* 1961 *and in revised form* 19 *April* 1961)

The structural properties of several compositions in the quarternary system $PbTiO_3$–$BaTiO_3$–$BaNb_2O_6$–$PbNb_2O_6$, formed by high temperature solid state reaction of the constituent oxides, have been studied by the X-ray powder diffraction technique. Phases isomorphous with (i) cubic perovskite, (ii) tetragonal barium titanate, (iii) orthorhombic barium titanate, (iv) cubic pyrochlore, (v) orthorhombic lead niobate, (vi) tetragonal tungsten-bronze and (vii) orthorhombic barium niobate have been identified. The respective region of stability of each phase has been depicted on a two-dimensional phase-diagram.

Titanates and niobates of barium and lead are important ferroelectric materials and their structural and dielectric properties have been studied in detail (Känzig, 1957; Megaw, 1957). Some binary solid solutions of these compounds such as $BaTiO_3$–$PbTiO_3$ (Shirane & Suzuki, 1951; Shirane & Takeda, 1951), $PbTiO_3$–$PbNb_2O_6$ (Subba Rao, 1960), $BaTiO_3$–$BaNb_2O_6$ (Subba Rao & Shirane, 1959), and $PbNb_2O_6$–$BaNb_2O_6$ (Fran-

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* N.C.L. Contribution No. 440.