THERMODYNAMIC PROPERTIES OF TERNARY REFRACTORY CARBIDES. III. ZIRCONIUM-HAFNIUM-CARBON

M. Hoch, et al

Cincinnati University
Cincinnati, Ohio

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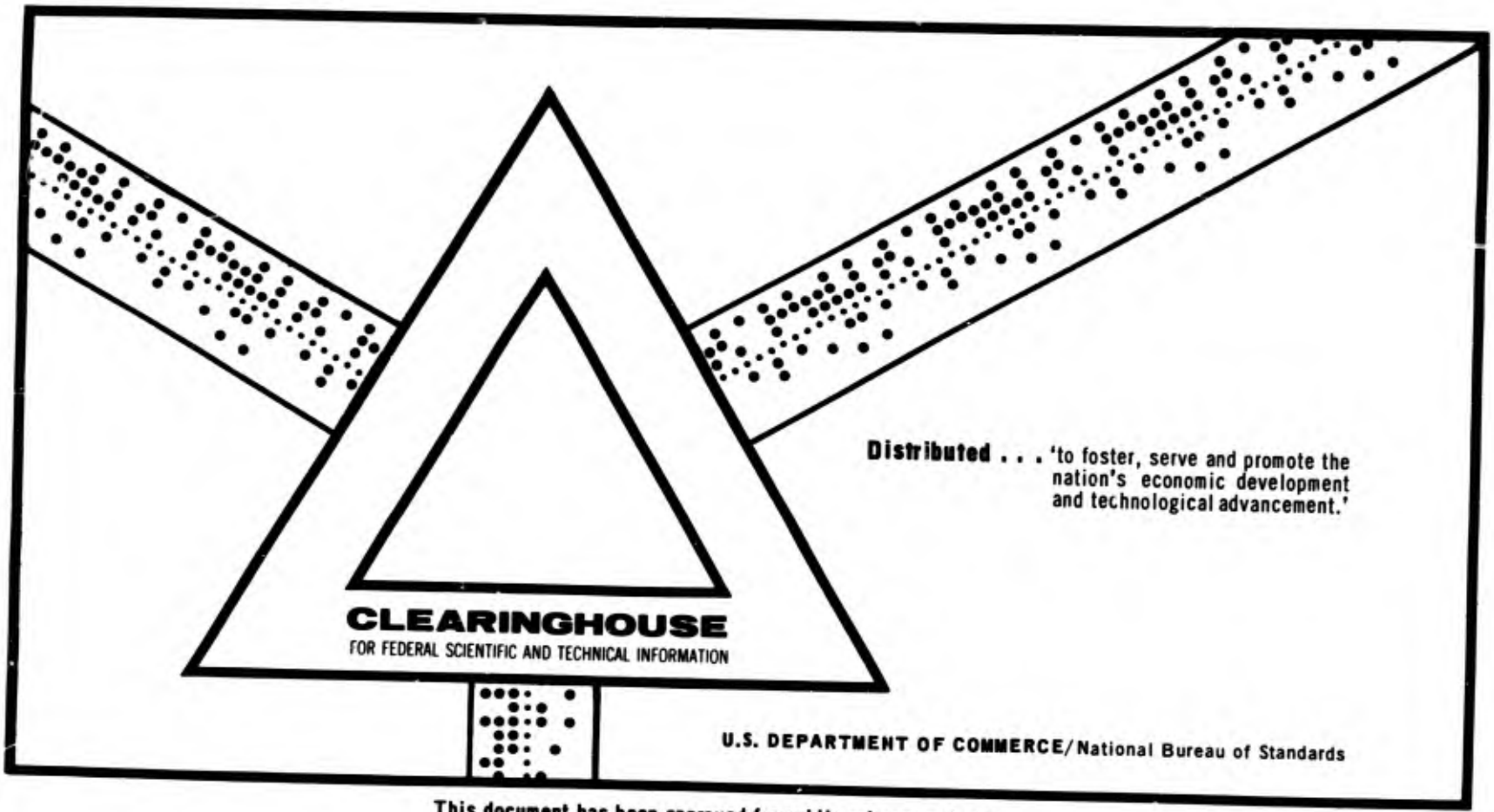

AFML-TR-69-209
PART III

THERMODYNAMIC PROPERTIES OF TERNARY REFRACTORY CARBIDES

III. ZIRCONIUM-HAFNIUM-CARBON

M. HOCH and S. YAMAUCHI

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AIR FORCE SYSTEMS COMMAND
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III. ZIRCONIUM-HAFNIUM-CARBON

M. HOCH and S. YAMAUCHI

FOREWORD

This report was prepared by the University of Cincinnati under Contract No. F33615-67-C-1565. This work was initiated under Project No. 7360, "Chemical, Thermal, and Dynamic Properties of Materials," Task 736005, "Compositional, Atomic, and Molecular Analysis." This research was supported in part by the National Aeronautics and Space Administration Research Grant NGR 36-004-014. The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command with Mr. Freeman F. Bentley as Project Engineer.

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The work was performed at the Materials Science Laboratory at Wright-Patterson Air Force Base, with Dr. Michael Hoch serving as the Principal Investigator.

This report has been reviewed and is approved.

Freeman F. Bentley

FREEMAN F. BENTLEY
Chief, Analytical Branch
Materials Physics Division
Air Force Materials Laboratory

ABSTRACT

The thermodynamic properties of ternary zirconium-hafnium carbide, $Zr_xHf_{1-x}C_y$, having the sodium-chloride type structure were studied, using the time-of-flight mass spectrometer. The ratios of the activities of the components were measured as a function of composition at 2440°K. From the variation of the ratio of activities with composition, the pairwise interaction energies were obtained. The metal-metal interaction energy $[E_{12} - \frac{E_{11}+E_{22}}{2}] = 1.9\pm0.3$ kcal/mole, similar to that in the body-centered cubic zirconium-hafnium metallic system. The difference between the zirconium-carbon and hafnium-carbon interaction energy $E_{13}-E_{23}$ is a function of composition and can be expressed as: $E_{13}-E_{23} = 9.8\pm0.05-[7.5\pm0.2]x$ in kcal/mole.

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I. INTRODUCTION

The importance of the role of the pairwise energies on the stability of compounds that deviate grossly from stoichiometry has been emphasized.[1-4] Hoch[4] has discussed the interaction energies in binary carbides.

However, information on the thermodynamic properties in ternary carbides is not abundant enough to extend the theory of non-stoichiometry to ternary systems. The purpose of this study is to obtain information on the activities of the components and to evaluate the pairwise interaction energies in the Zr-Hf-C ternary system.

II. THEORY

The Zr-Hf-C ternary system has a fairly wide single phase region with the sodium-chloride type structure. The metal sites form an f.c.c. sublattice and are randomly filled with Zr and Hf atoms; some of the C sites, which also form f.c.c. sublattices, are empty. The general formula for this system, therefore, can be written as $Zr_xHf_{1-x}C_y$, where $0 \leq x \leq 1$, $0 < y < 1$.

The grand partition function for this type of system has been given by Jun:[5]

$$GPF = \sum \frac{N!}{N_1!\,(N-N_1)!} \cdot \frac{N!}{N_3!\,(N-N_3)!} [a_1K_1(T)]^{N_1} [a_2K_2(T)]^{N-N_1}$$
$$[a_3K_3(T)]^{N_3} \exp[-\frac{1}{kT}(N_1E_1 + N_2E_2 + N_3E_3 + \frac{N_1^2}{2N} E_{11} +$$
$$\frac{N_2^2}{2N} E_{22} + \frac{N_3^2}{2N} E_{33} + \frac{N_1N_2}{N} E_{12} + \frac{N_1N_3}{N} E_{13} + \frac{N_2N_3}{N} E_{23})] \quad (1)$$

where N is the number of available metal (and also carbon) sites and N_i is the number of atoms present; a_i is the absolute activity of each component in the crystal phase; $K_i(T)$ is the contribution of an added atom to the partition function for the normal vibrational modes of the crystal; E_i is the energy required to bring an atom from its standard state into the sodium-chloride type lattice; and E_{ij} is the pairwise interaction energy. Subscript 1 refers to Zr, 2 to Hf, and 3 to C.

By the usual treatment,[5] the following equations are obtained:

$$RT\ln a_1 = RT\ln x(1-y) + E_1 + (1-x)^2[E_{12} - \tfrac{1}{2}(E_{11}+E_{22})] + \frac{E_{11}}{2} + (1-x)y\,E_{13} - (1-x)y\,E_{23} - \tfrac{1}{2}y^2E_{33} - RT\ln K_1(T) \quad (2)$$

$$RT\ln a_2 = RT\ln(1-x)(1-y) + E_2 + x^2[E_{12} - \tfrac{1}{2}(E_{11}+E_{22})] + \frac{E_{22}}{2} + xy(E_{23}-E_{13}) - \tfrac{1}{2}y^2\,E_{33} - RT\ln K_2(T) \quad (3)$$

$$RT\ln a_3 = RT\ln\frac{(1-y)}{y} + E_3 + y\,E_{33} + x\,E_{13} + (1-x)E_{23} - RT\ln K_3(T) \quad (4)$$

where $x = \frac{N_1}{N}$, $1-x = \frac{N_2}{N}$, and $y = \frac{N_3}{N}$.

Combining equations (2), (3), and (4), the following equations are obtained:

$$RT\ln\frac{a_1}{a_2}\cdot\frac{1-x}{x} = E_1 - E_2 + (1-2x)[E_{12} - \tfrac{1}{2}(E_{11}+E_{22})] + \tfrac{1}{2}[E_{11}-E_{22}] + y[E_{13}-E_{23}] - RT\ln\frac{K_1(T)}{K_2(T)}. \quad (5)$$

$$RT\ln\frac{a_1}{a_3}\cdot\frac{y}{x(1-y)^2} = E_1 - E_3 + \frac{E_{11}}{2} - E_{13} + (1-x)(1+y)[E_{13}-E_{23}] + (1-x)^2[E_{12} - \tfrac{1}{2}(E_{11}+E_{22})] - (y + \frac{y^2}{2})E_{33} - RT\ln\frac{K_1(T)}{K_3(T)}. \quad (6)$$

$$RT\ln \frac{a_2}{a_3} \cdot \frac{y}{(1-x)(1-y)^2} = E_2 - E_3 + \frac{E_{22}}{2} - E_{23} + x(1+y)[E_{23}-E_{13}]$$

$$+ x^2[E_{12} - \tfrac{1}{2}(E_{11}+E_{22})] - (y + \frac{y^2}{2})E_{33} - RT\ln \frac{K_2(T)}{K_3(T)}. \qquad (7)$$

Equations (5) and (6) and (7) are used to evaluate the pairwise interaction energies.

III. PREVIOUS INVESTIGATIONS

The phase relationships in the Zr-C and Hf-C systems have been reviewed by Storms.[6] The available thermodynamic data on Zr-C were evaluated by Hoch[4] and Jun.[5]

The high temperature evaporation data of HfC_y were used by Hoch[4] to evaluate the activity of Hf and C in HfC_y as:

$$RT\ln a_{Hf} \cdot \frac{1}{1-y} = (1\pm1)-(7.5\pm4)y^2 \text{ kcal/mole.}$$

$$RT\ln a_{C} \cdot \frac{1-y}{y} = -(47\pm10)+(15\pm8)(1-y) + 2\times10^{-3}T \text{ kcal/mole.}$$

Assuming $\Delta H_f = \Delta E_f$, ΔH_f, the heat of formation of HfC_y can be expressed as:

$$\Delta H_f = (1\pm1)-(62\pm18)y+(7.5\pm4)y^2 \text{ kcal/mole.} \qquad (8)$$

This value is compared in Figure 1 ($\frac{\Delta H_f}{y}$ versus composition) together with values obtained by combustion calorimetry.

At higher carbon content, the values of Hoch,[4] Mah,[7] and Zhelankin and Kutsev[8] are in good agreement. At lower carbon content, the difference between the values calculated by Hoch[4] and measured by Zhelankin and Kutsev[8] increases. Zhelankin and Kutsev's data show a large composition dependence, giving a very large pairwise interaction energy. A straight line through Zhelankin and Kutsev's data in Figure 1 gives for ΔH_f

$$\Delta H_f \simeq -118\ y + 64\ y^2.$$

A carbon pairwise interaction energy $\frac{E_{33}}{2}$ of 64 kcal/mole seems too high,[4] similarly a value of -118 kcal/mole for (E_3+E_{23}).

IV. EQUIPMENT AND MATERIALS

The same equipment as used by Jun[5] was employed.

Carbon powder of 99.9999%, zirconium oxide of 99.95%, and hafnium oxide of 98.95% were obtained from Atomergic Chemetals Company, Division of Gallard-Schlesinger Chemical Manufacturing Corporation, Carle Place, Long Island, New York.

V. EXPERIMENTAL PROCEDURE

A. Preparation of Samples

$Zr_xHf_{1-x}C_y$ was prepared by mixing zirconium oxide, hafnium oxide, and carbon, and reacting them as described by Jun.[5]

B. Mass Spectrometer Operation

The mass spectrometer was used as described by Jun.[5]

There are five stable isotopes of zirconium; Zr^{90} (51.46%), Zr^{91} (11.23%), Zr^{92} (17.11%), Zr^{94} (17.40%), and Zr^{96} (2.8%). The intensity of Zr^{90} (51.46% natural abundance) was measured for zirconium.

There are four stable isotopes of hafnium; Hf^{177} (18.5%), Hf^{178} (27.1%), Hf^{179} (13.8%), and Hf^{180} (35.2%). The intensity of all four isotopes was measured and converted into the values of Hf^{180} using relative abundances. The average of these values was used in the calculations.

Intensity of C^{12} (natural abundance 98.89%) was measured for carbon peak.

VI. RESULTS AND DISCUSSION

The nominal composition of the samples along with the lattice parameters is shown in Table I. The lattice parameter was determined by the Nelson-Riley extrapolation method;[9] their accuracy is ±0.001Å.

The lattice parameters in the ternary system, $Zr_xHf_{1-x}C_y$, show an almost linear dependence on metal composition as shown in Figures 2, 3, and 4. The data agree with those of Nowotny, et al.,[10] Samsonov, et al.,[11] and Gladyshevskii, et al.;[12] ($y \simeq 1.0$).

The mass spectrometric experiments were carried out at 2570°K.

The partial pressure P_i of chemical species i is related to the ion current I_i as follows:

$$K_i P_i = I_i T \tag{10}$$

where K_i is a constant. Therefore, the ratio of partial pressure of Zr to that of Hf is expressed as follows:

$$\frac{P_{Zr}}{P_{Hf}} = \frac{K_{Zr} I_{Zr}}{K_{Hf} I_{Hf}} = C' \frac{I_{Zr}}{I_{Hf}} = C \frac{I_{Zr}90}{I_{Hf}180} \tag{11}$$

where $C' = K_{Zr}/K_{Hf}$ is a constant. I_{Zr} and I_{Hf} designate total ion current of Zr and Hf, respectively. $I_{Zr}90$ and $I_{Hf}180$ designate the ion current of Zr^{90} and Hf^{180}, respectively.

Using equation (11), equation (5) is rewritten as:

$$RT\ln \frac{I_{Zr}^{90}}{I_{Hf}^{180}} \cdot \frac{1-x}{x} = (1-2x)\left[E_{12} - \tfrac{1}{2}(E_{11}+E_{22})\right] + y[E_{13}-E_{23}] + (E_1-E_2) + \tfrac{1}{2}[E_{11}-E_{22}] - RT\ln \frac{K_1(T)}{K_2(T)} - RT\ln C \frac{P^{\circ}_{Hf}}{P^{\circ}_{Zr}}. \qquad (12)$$

Measured intensities of ratios are given in Table II.

The slope of a plot of $RT\ln \frac{I_{Zr}^{90}}{I_{Hf}^{180}} \cdot \frac{1-x}{x}$ versus $(1-2x)$ with y constant gives $[E_{12} - \frac{1}{2}(E_{11}+E_{22})]$. The data are shown in Figure 5.

A least squares analysis gives $E_{12} - \frac{1}{2}[E_{11}+E_{22}] = 1.86 \pm 0.30$ kcal/mole.

Plotting $RT\ln \frac{I_{Zr}^{90}}{I_{Hf}^{180}} \cdot \frac{1-x}{x}$ versus y and holding x constant, gives a straight line. The slope of this straight line, $[E_{13}-E_{23}]$, was calculated by least squares and is given in Table IV. $[E_{13}-E_{23}]$ depends linearly on x as shown in Figure 6 and can be expressed as $[E_{13}-E_{23}] = [9.6\pm0.8]-[7.8\pm0.2]x$ kcal/mole.

For each intensity ratio in Table II, each peak was measured ten times and the average of the readings used to calculate the ratio.

Kubachewski,[13,14] assuming ideal solution for Zr-Hf binary alloys, calculated the solidus and the liquidus curves for Zr-Hf phase diagram. The results showed fairly good agreement with experimentally determined phase relationships. The

above result shows that the Zr-Hf binary alloy is an ideal solution, therefore, $[E_{12} - \frac{1}{2}(E_{11}+E_{22})] \simeq 0$ for the Zr-Hf b.c.c. metallic solution.

This value is of the same order of magnitude, as obtained in this study for the metal sublattice in the carbide; $E_{12} - \frac{1}{2}(E_{11}+E_{22}) = 1.86 \pm 0.3$ kcal/mole.

$[E_{13}-E_{23}]$, the difference in bonding between Zr-C and Hf-C shows a linear relationship with composition. This fact and the bonding in carbides will be discussed in a subsequent paper.

TABLE I

Lattice Parameters of $Zr_xHf_{1-x}C_y$ in Å

Composition $Zr_xHf_{1-x}C_y$		Lattice Parameter
x	y	Å
0	0.82	4.633
	0.87	4.638
	0.96	4.640
0.2	0.82	4.647
	0.87	4.651
	0.96	4.652
0.5	0.82	4.665
	0.87	4.668
	0.96	4.670
0.8	0.82	4.684
	0.87	4.689
	0.96	4.691
1.0	0.82	4.700
	0.87	4.700
	0.96	4.698

TABLE II

Ion Intensity Ratios

Composition	$\frac{I_{Zr}}{I_{Hf}}$	Composition	$\frac{I_{Zr}}{I_{Hf}}$
$Zr_{.2}Hf_{.8}C_{.82}$	0.7092	$Zr_{.5}Hf_{.5}C_{.96}$	2.3674
	0.6494		2.0572
	0.5562		2.3624
	0.5774		2.3975
	0.5322		2.2002
			2.0859
$Zr_{.2}Hf_{.8}C_{.87}$	0.7089		
	0.7084	$Zr_{.8}Hf_{.2}C_{.82}$	6.0423
	0.6408		7.3529
	0.6127		6.6756
	0.5351		6.7889
	0.5399		6.7935
$Zr_{.2}Hf_{.8}C_{.96}$	0.7874	$Zr_{.8}Hf_{.2}C_{.87}$	7.5758
	0.9847		5.3999
	0.8425		6.5625
	0.9211		5.5512
	0.5612		4.2668
	0.6309		6.0976
	0.5800		
	0.6821	$Zr_{.8}Hf_{.2}C_{.96}$	5.9524
			6.1576
$Zr_{.5}Hf_{.5}C_{.82}$	1.7705		6.9735
	1.8829		7.4349
	1.9334		8.4746
	1.7947		
	1.7039		
	1.8549		
$Zr_{.5}Hf_{.5}C_{.87}$	2.6420		
	3.1319		
	2.7285		
	2.6344		
	2.4260		
	2.3488		
	2.1943		
	2.9041		

TABLE III

Calculated Pairwise Interaction Energies in $Zr_xHf_{1-x}C_y$

Composition x	$[E_{13}-E_{23}]$ kcal/mole
0.2	7.9±5.8
0.5	5.9±7.1
0.8	3.2±2.1

$[E_{12}-\frac{1}{2}(E_{11}+E_{22})] = 1.86\pm0.30$ kcal/mole

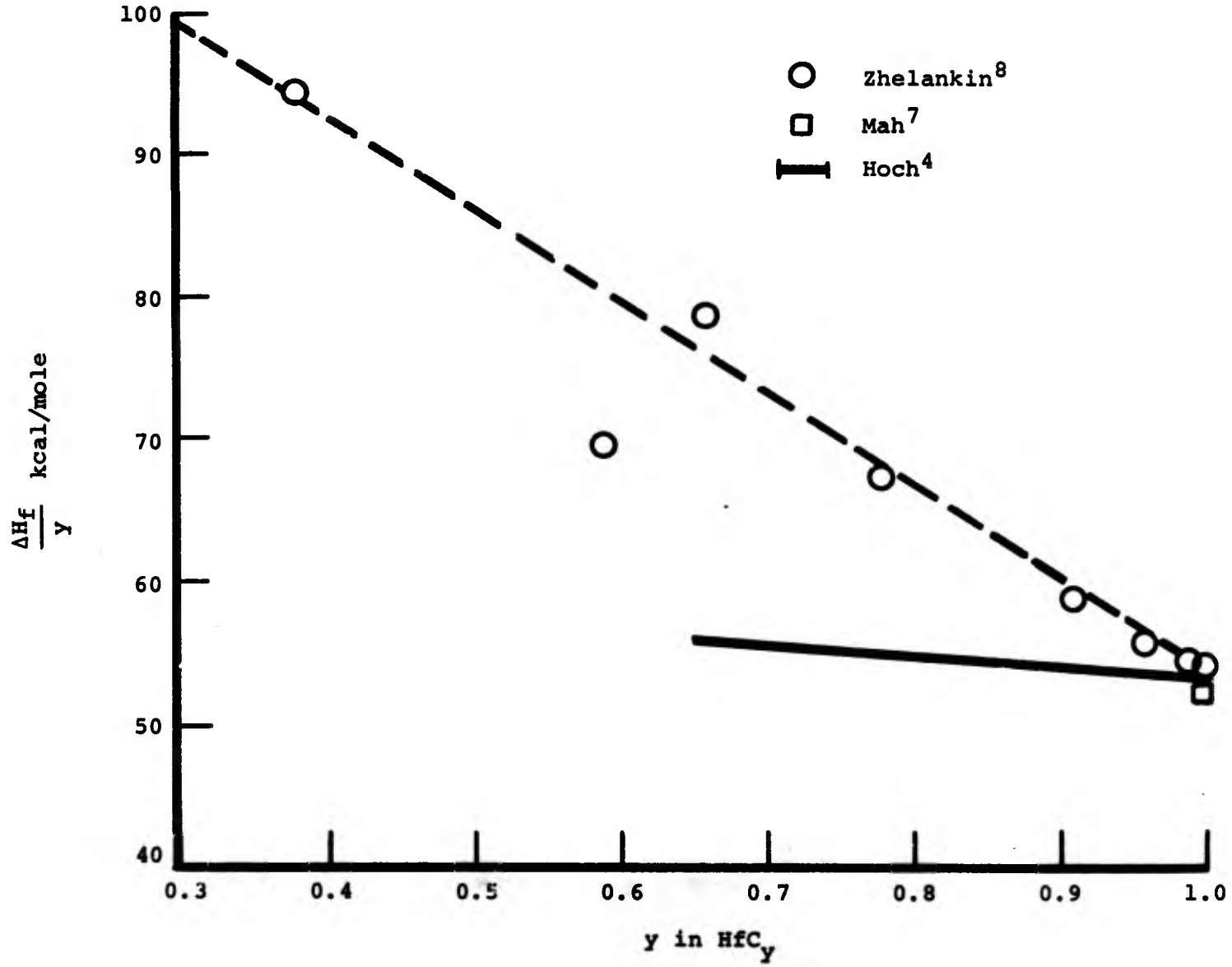

Fig. 1. Heat of Formation of HfC_y

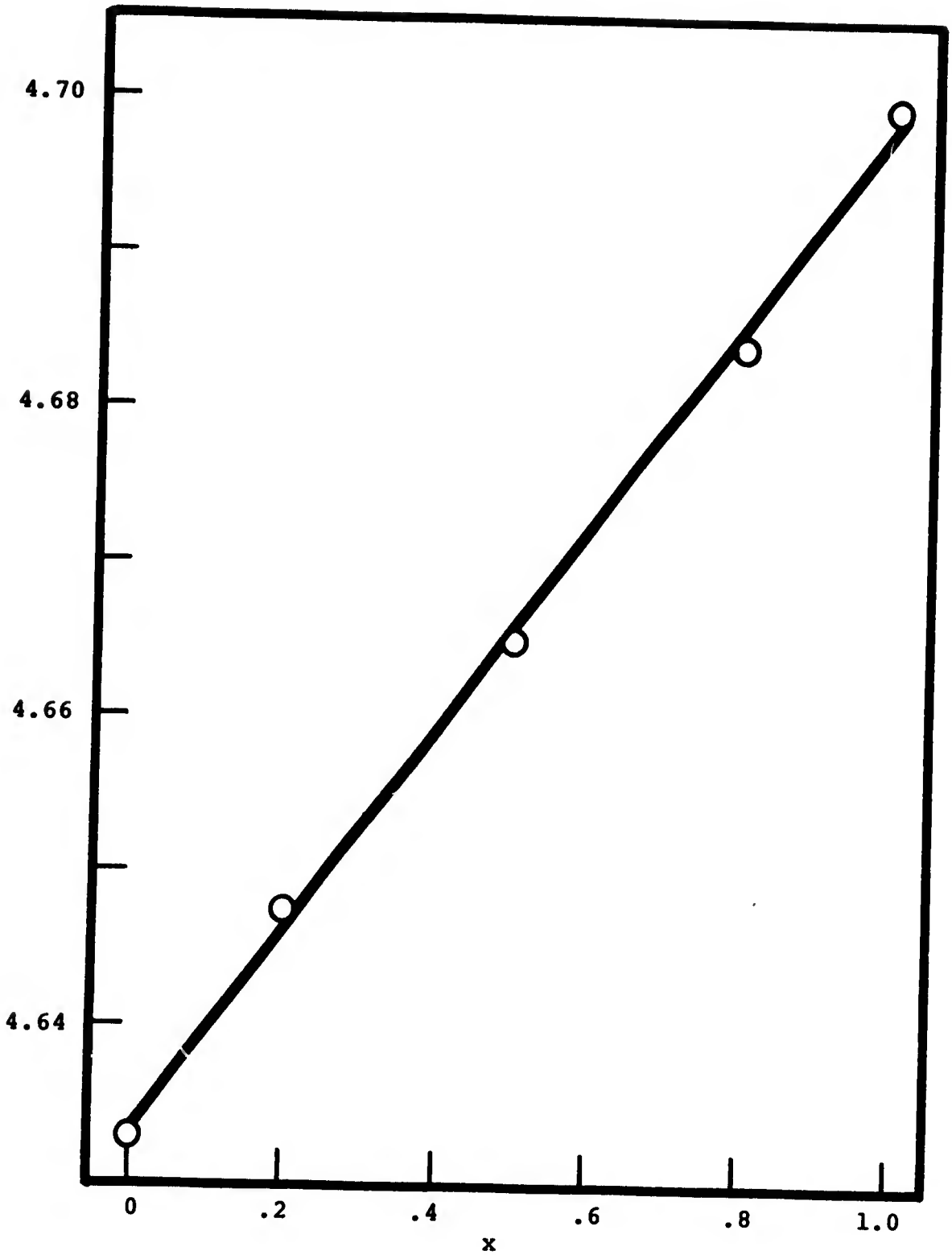

Fig. 2. Lattice Parameters of $Zr_xHf_{1-x}C_{0.82}$

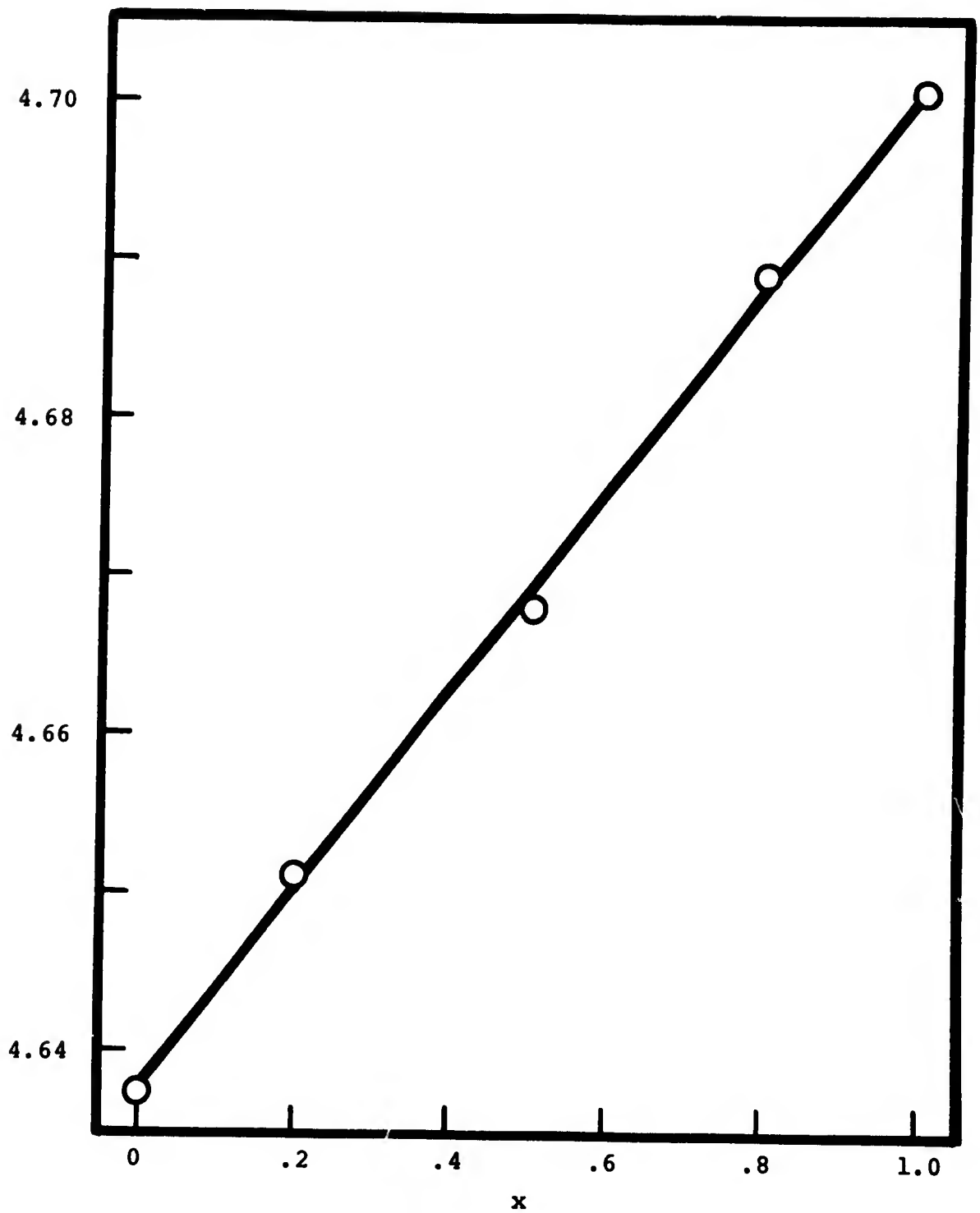

Fig. 3. Lattice Parameters of $Zr_xHf_{1-x}C_{0.87}$

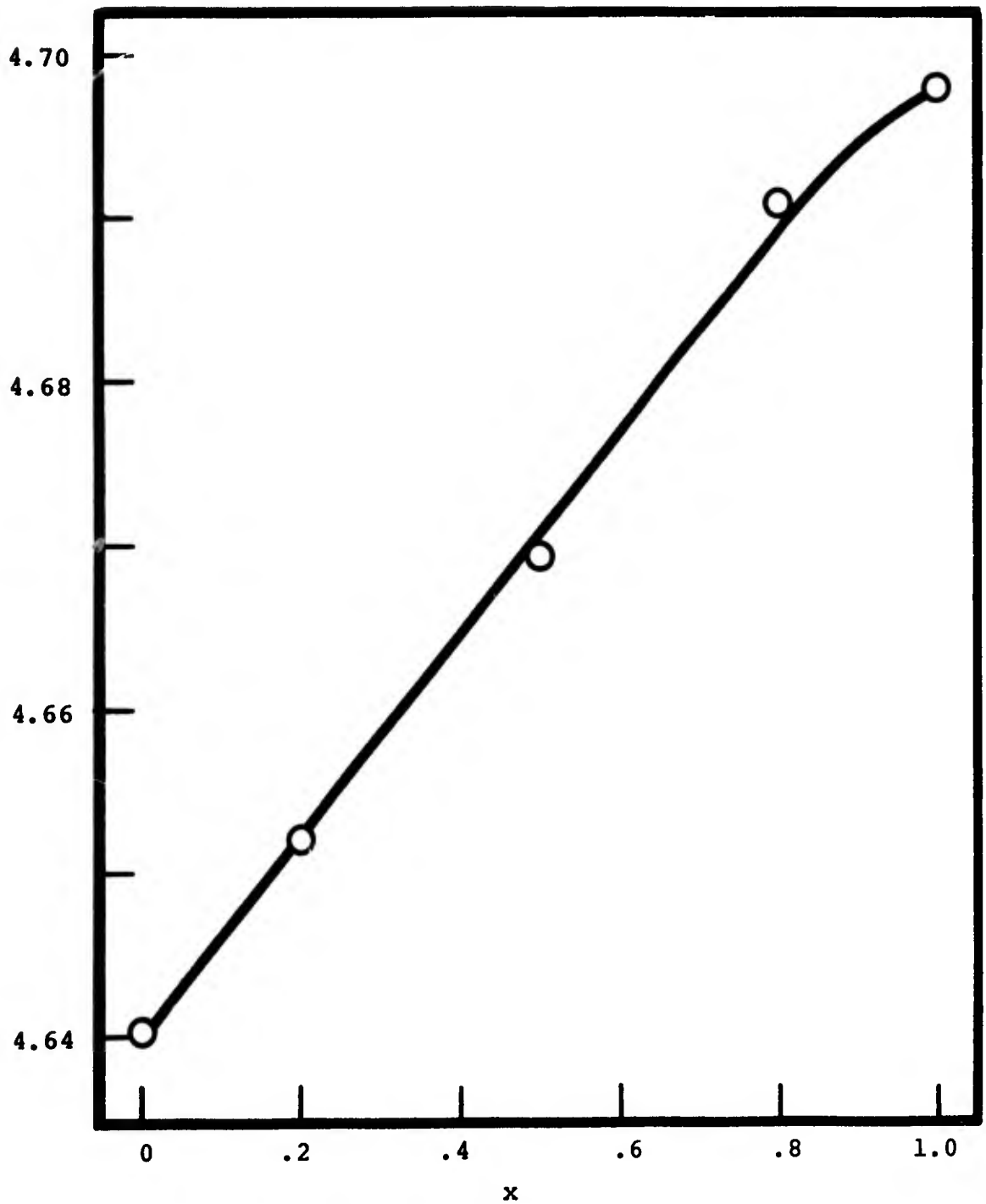

Fig. 4. Lattice Parameters of $Zr_xHf_{1-x}C_{0.96}$

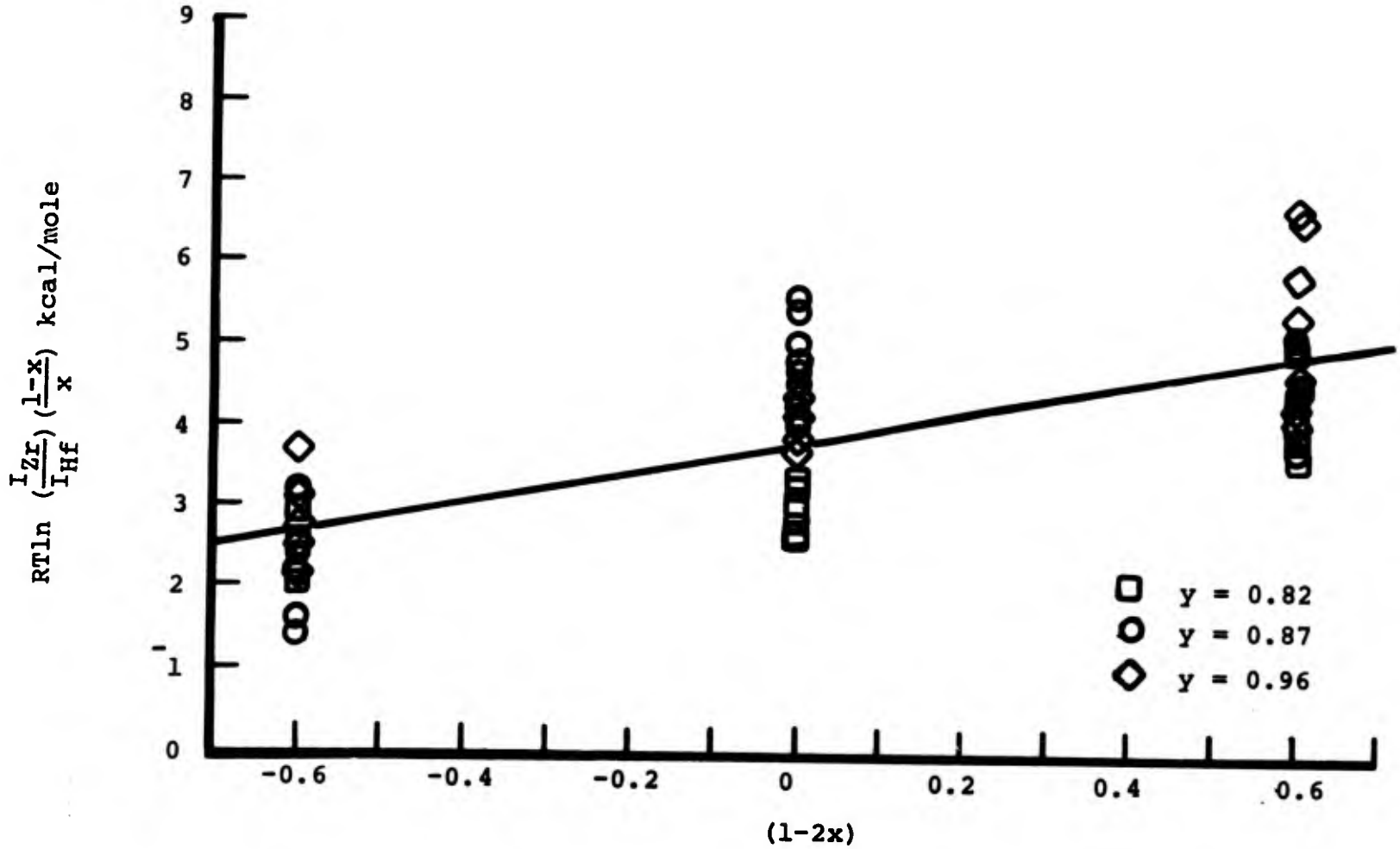

Fig. 5. Evaluation of $E_{12} - [\frac{E_{11}+E_{22}}{2}]$ in $Zr_xHf_{1-x}C_y$

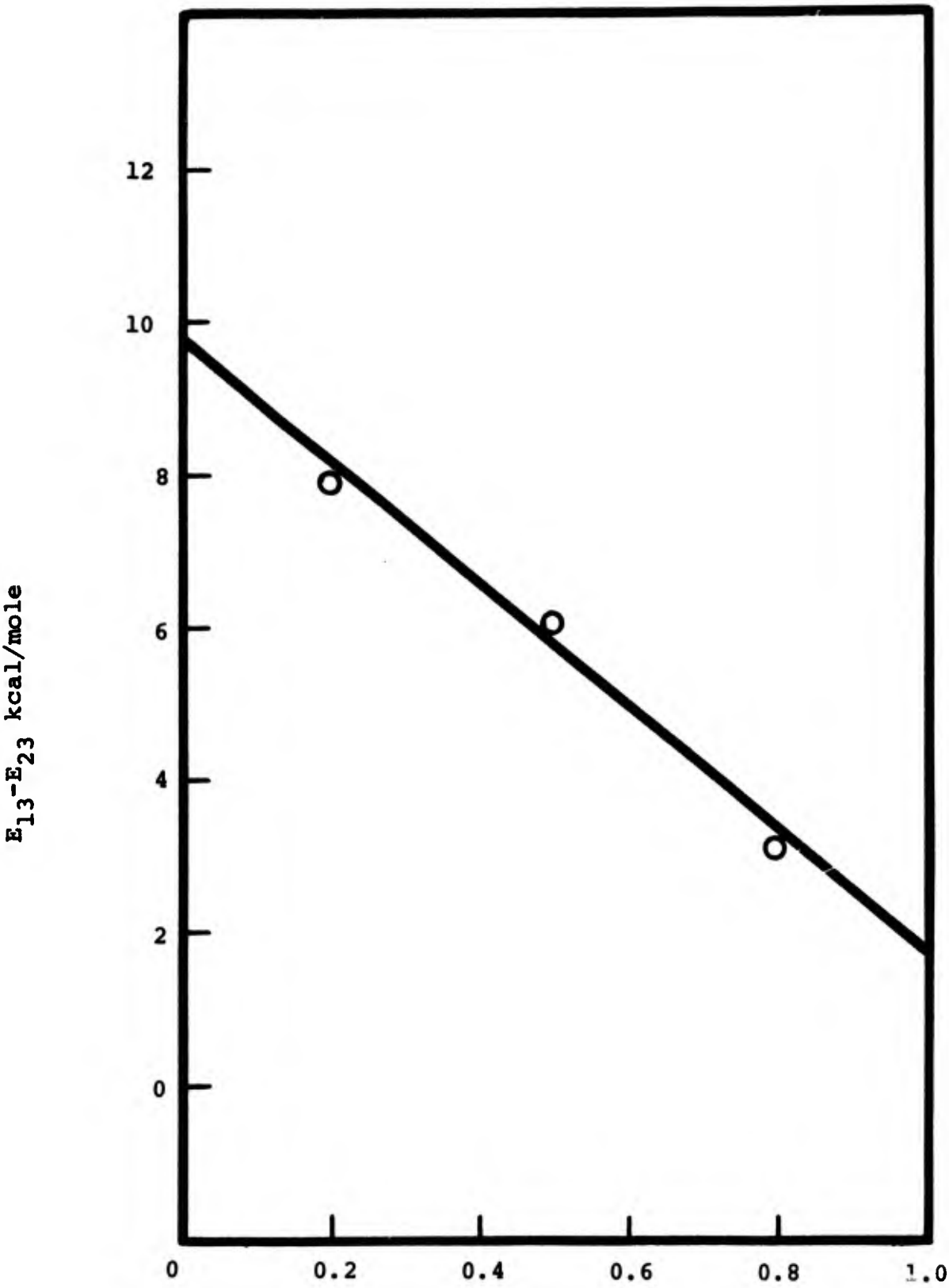

Fig. 6. Variation of E_{13}-E_{23} with Composition in $Zr_xU_{1-x}C_y$

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13. ABSTRACT

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