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## Densities of Metal-Metalloid Amorphous Alloys\*

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## Synopsis

Binary, ternary and quaternary Fe-, Co- and Ni-base amorphous alloys containing metalloid elements of B, Si or P were produced by a melt quenching technique. Densities of these amorphous alloys were measured by the liquid displacement method using tetrabromoethane ( $\text{Br}_2\text{CHCHBr}_2$ ). The concentration dependence of the densities, in particular the metalloid concentration effect, indicates that the structural features of amorphous alloys with lower metalloid concentration differ slightly from those of higher metalloid concentration alloys. This is consistent with the concept of two amorphous structure recently suggested as a novel picture for the structure of amorphous alloys. The effect of replacing metallic elements on the structural features is less sensitive than the changes as a function of metalloid concentration.

## I Introduction

According to the suggestion of Polk<sup>1)</sup>, Bennett<sup>2)</sup>, Cargill<sup>3)</sup>, Ichikawa<sup>4)</sup> and others, the structure of amorphous metals may be characterized by the dense random packing (DRP) of hard spheres<sup>5)</sup>. Along this line, Ray et al.<sup>6)</sup> explained the concentration dependence of the density of binary Fe-B amorphous alloys by a model structure in which unfilled Fe and B sites will occur for  $B \geq 20$  at% and  $B < 20$  at%, respectively.

Densities for some amorphous alloys, such as Ni-P<sup>7)</sup>, Fe-P<sup>8)</sup>, Co-P<sup>3)</sup>, (Fe and Co)-(P, C, Si or B)<sup>9)</sup> and  $(\text{Fe, Co and Ni})_{77}\text{Si}_{10}\text{B}_{13}$ <sup>10)</sup> are reported with an uncertainty of about 0.5 ~ 1%<sup>6,10)</sup>. Accurate density data may give a possible explanation on the structural features of amorphous alloys.

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In the density measurement for amorphous ribbon by the Archimedean method, there are two important problems; the elimination of bubbles in liquid and the good contact between sample and liquid. These two problems are easily overcome by using tetrabromoethane  $\text{Br}_2\text{CHCHBr}_2$  with the high specific gravity and the non-volatility at room temperature.

The main purpose of this work is to present the density for some amorphous alloys of the (Fe, Co or Ni)-(Si, B or P) systems systematically measured by the Archimedean method with tetrabromoethane and to discuss the structural features including the first nearest neighbour distance on the basis of these density data and the results by X-ray diffraction.

## II Experimental

Several binary, ternary and quaternary Fe-, Co- and Ni-base amorphous alloys containing metalloid elements were made by a single-roller quenching method. These samples were in the form of ribbons (about 40  $\mu\text{m}$  thick, 1 mm wide). Density measurement of these amorphous alloys was carried out as follows;

First, weight of the sample ( $W_S$ ) and a standard Ni bulk sample ( $W_{\text{Ni}}$ ) were measured in air. Next, weights of the sample plus sample holder ( $W'_S$ ), sample holder only ( $W'_h$ ) and Ni sample plus sample holder ( $W'_{\text{Ni}}$ ) were measured in  $\text{Br}_2\text{CHCHBr}_2$  using a microbalance with a sensitivity of 0.001 mg. Care was also taken to eliminate the air bubbles from the fluid.

Density of samples (D) was calculated from the following relation,

$$D = \frac{W_S}{W_{\text{Ni}}} \cdot \frac{W_{\text{Ni}} - (W'_{\text{Ni}} - W'_h)}{W_S - (W'_S - W'_h)} \cdot D_{\text{Ni}} \quad (1)$$

where  $D_{\text{Ni}}$  is the density of standard Ni.

In this measurement, the correction for temperature difference is negligible, because, the absolute value of D is reduced by comparing with the  $D_{\text{Ni}}$  and the volume expansion coefficient of Ni is the order of  $10^{-5}$  /deg.

The uncertainty of density obtained with distilled  $\text{Br}_2\text{CHCHBr}_2$ ,  $\text{H}_2\text{O}$  and  $\text{CCl}_4$  as the liquid in the Archimedean principle is shown in Table I. The values of uncertainty (in %) in this table are obtained as an average of five observations for a  $\text{Co}_{72}\text{B}_{28}$  binary amorphous ribbon alloy. As shown in the table, for a small sample of about 50 mg, an uncertainty in this measurement is smaller than about 0.1% with  $\text{Br}_2\text{CHCHBr}_2$ . In this work, sample weight used in density measurement is about 70 ~ 120 mg.

Table I The uncertainty (%) of density measurement for amorphous  $\text{Co}_{72}\text{B}_{28}$  alloy with three different liquids by the Archimedeian method.

Liquid		$\text{H}_2\text{O}$	$\text{CCl}_4$	$\text{Br}_2\text{CHCHBr}_2$
Density ( $\text{g}/\text{cm}^3$ , 20 °C)		0.9982	1.5947	2.955
Sample weight (mg)	25	1.6	0.7	0.2
	50	1.3	0.2	0.08
	100	0.3	0.1	0.05
	700	0.1	0.01	0.01

### III Results and discussion

Concentration dependence of density  $D$  (in  $\text{g}/\text{cm}^3$ ) in binary  $\text{Fe}_{1-x}\text{P}_x$  ( $x = 0.145 \sim 0.20$ ),  $\text{Fe}_{1-x}\text{B}_x$  ( $x = 0.12 \sim 0.24$ ) and  $\text{Co}_{1-x}\text{B}_x$  ( $x = 0.16 \sim 0.31$ ) amorphous alloys is given in Fig. 1. The absolute values of  $D$  for Fe-P alloys obtained in this work are in good agreement with those of the previous works<sup>11,12</sup>). The  $D$  of Fe-B and Co-B alloys obtained in this work are lower by about 1 % than those reported by Hasegawa and Ray<sup>6,12,13</sup>). Although no definite reason is available at the present time, probably the uncertainty of the density measurement may account for part of the difference. We may also suggest that the present method is very sensitive to the small density change. However, a slight

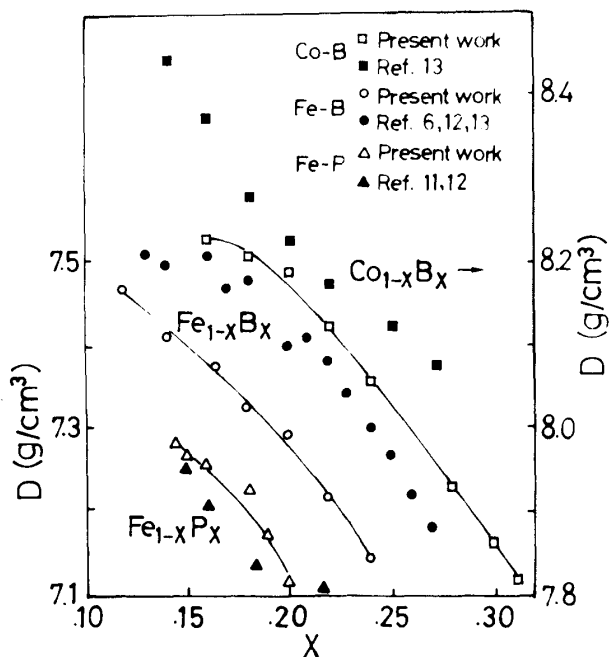


Fig. 1 Densities of Fe-P Fe-B and Co-B binary amorphous alloys.

deviation from the linear relation between density and concentration is found near the composition range of 20 at% B in both Fe-B and Co-B alloys. This is consistent with the previous results<sup>11-13)</sup> for Fe-B alloys.

The density of one metal and two metalloid amorphous alloys are given in Fig. 2. The density of Fe-P-B alloys containing fixed B decrease with increasing P concentration. The density of Co-Si-B alloys containing fixed Si decrease slowly with increasing B concentration and then more rapidly. The concentration of 13 at% at which there is a change in a slope in Co-Si-B alloys, is lower than the case of 20 at% B in Co-B alloys in Fig. 1.

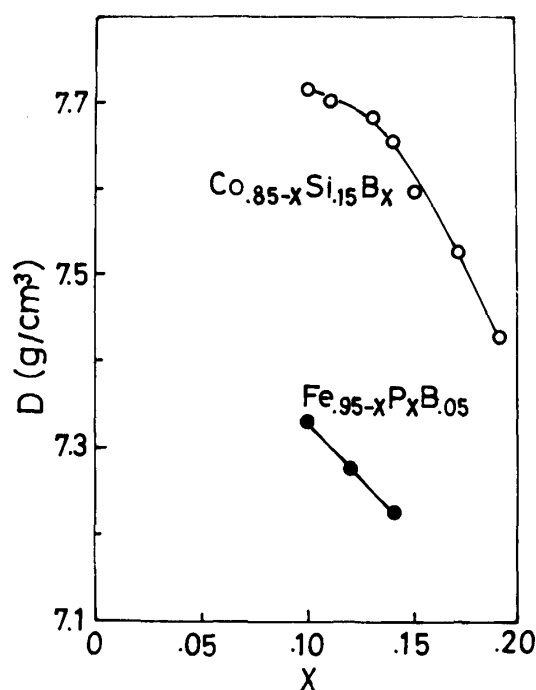


Fig. 2 Densities of metal-two metalloid amorphous alloys containing a fixed concentration of one metalloid.

Concentration dependence of the density for Co-Ni, Fe-Ni and Fe-Co amorphous alloys containing fixed concentration of metalloids is illustrated in Fig. 3. For  $(\text{Co}_{1-x}\text{Ni}_x)_{0.7}\text{Si}_{0.15}\text{B}_{0.15}$  alloys, the density decreases linearly with increasing Ni concentration from 7.6 to 7.54 g/cm<sup>3</sup>. For  $(\text{Fe}_{1-x}\text{Ni}_x)_{0.78}\text{Si}_{0.1}\text{B}_{0.12}$  and  $(\text{Fe}_{1-x}\text{Co}_x)_{0.75}\text{Si}_{0.15}\text{B}_{0.1}$  alloys, the density increases linearly with increasing x showing a slight upward bend at about  $x = 0.6$  and  $0.5$ , respectively. Comparing the results of Fig. 3 with those of Fig. 2, however, it is known that the effect of replacing metallic elements in the alloys with fixed metalloid concentration on the density is less sensitive than that of replacing metalloid elements in the alloys with fixed metal concentration. A similar behaviour has been reported by the systematic investigation on the

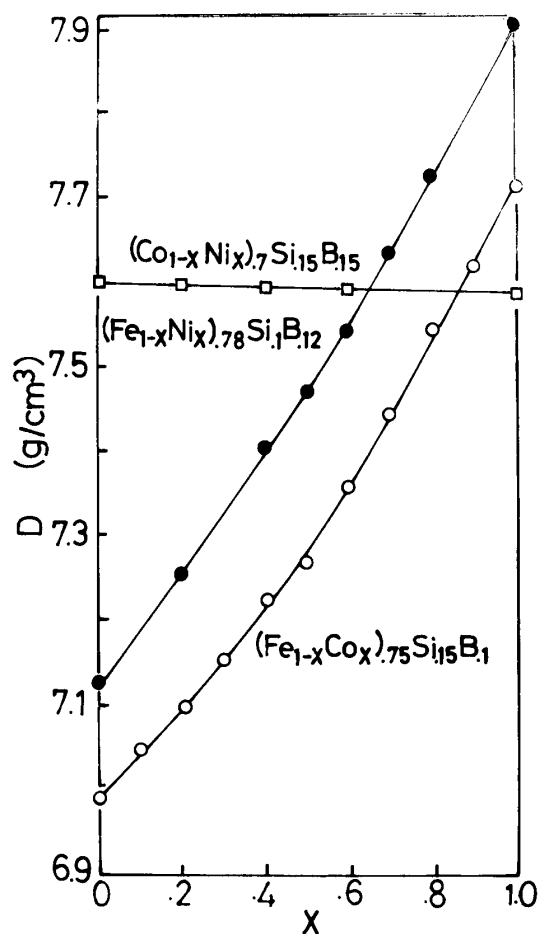


Fig. 3 Densities of Fe-Ni, Fe-Co and Co-Ni amorphous alloys containing a fixed concentration of metalloids.

structure of other amorphous alloys<sup>14,15</sup>).

The density must be related to the structural features of amorphous alloys, so that some various information can be deduced from the present measurements. The variation of mean atomic volume  $\bar{V}$  of each amorphous alloy is evaluated from the measured density and the average atomic weight. The results are given in Figs. 4 and 5 for Fe-B, Fe-P and Co-B alloys together with those of Co-P<sup>1)</sup> and Ni-P<sup>7)</sup> alloys.

It is distinguished that the values of  $\bar{V}$  show a linear dependence of the metalloid concentration of B or P. This feature is frequently found in crystalline phase with homogeneous range like solid solution. The extrapolated value of the mean atomic volume  $\bar{V}_0$  in the limit where  $x \rightarrow 0$  gives the volume of amorphous alloys containing no metalloid element. As shown in Fig. 4, both set of the  $\bar{V}$  data for two iron base amorphous alloys were expressed by the following equations using a least squares method;

$$\bar{V} = 12.10 - 7.20X \quad (A^3) \quad \text{for Fe-B} \quad (2)$$

$$\bar{V} = 12.10 - 1.00X \quad (A^3) \quad \text{for Fe-P} \quad (3)$$

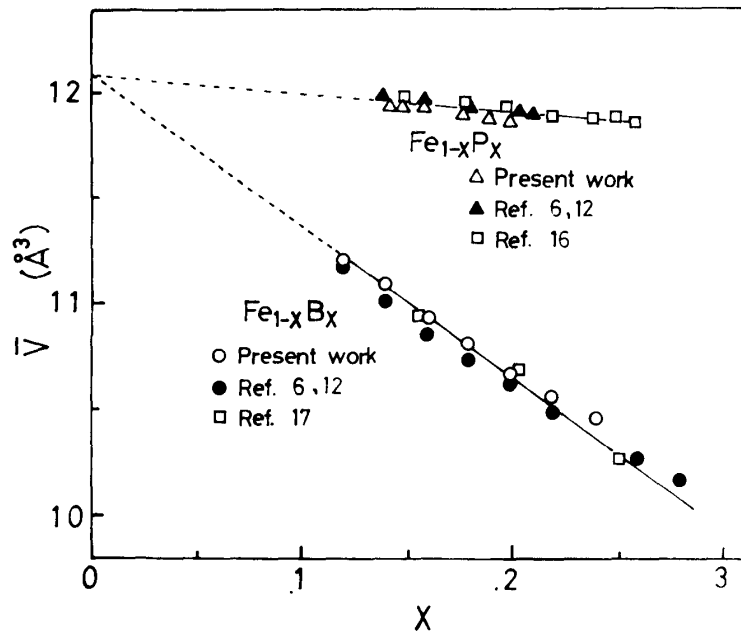


Fig. 4 Mean atomic volumes of Fe-B and Fe-P amorphous alloys

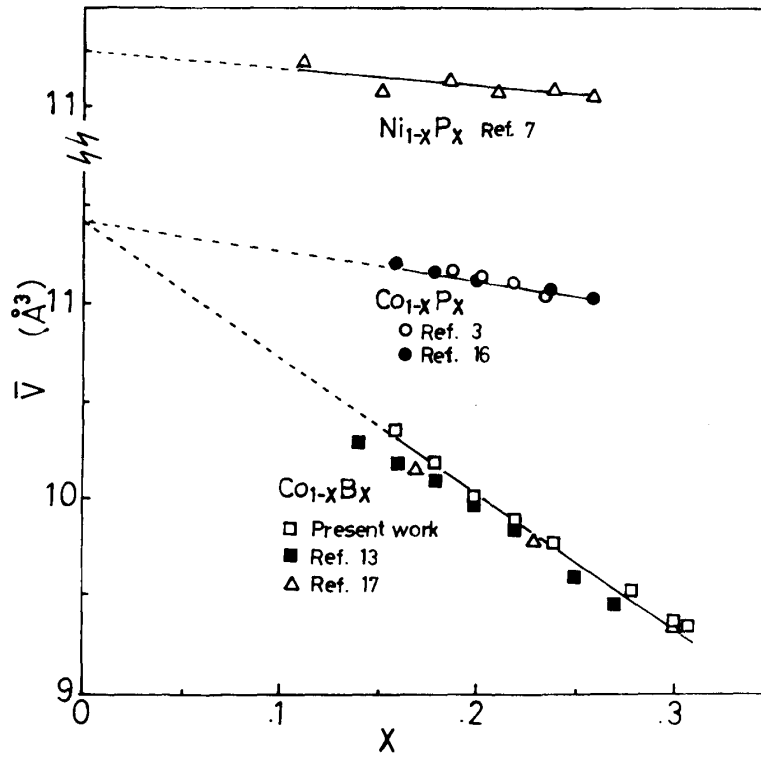


Fig. 5 Mean atomic volumes of Co-B, Co-P and Ni-P amorphous alloys.

where  $x$  is the metalloid concentration in atomic fraction.

From the eqs. (2) and (3), the  $\bar{V}_0$  of amorphous pure iron is  $12.10 \text{ \AA}^3$ . Since the mean atomic volume  $\bar{V}'_0$  in the crystalline iron is  $11.80 \text{ \AA}^3$ ,  $\bar{V}_0$  is larger than  $\bar{V}'_0$ , so that in the case of Fe the relative volume difference from the crystalline structure to the amorphous one is estimated to be 2.5 % by using the relation of  $(\bar{V}_0 - \bar{V}'_0)/\bar{V}'_0$ . The present value is the order of the volume change (1 ~ 5%) on melting. It should be noted that the mean atomic volume of  $\gamma$ -iron having the close packed structure is estimated to be  $11.32 \text{ \AA}^3$ , then the relative volume difference is found to be 6.9 % which is somewhat larger than the typical volume change (1 ~ 2%) on melting observed in the close packed metals.

Applying the similar analysis regarding the  $\bar{V}$  to other systems of Co-B, Co-P and Ni-P in Fig. 5, the following results were obtained.

$$\bar{V} = 11.42 - 6.99X \quad (\text{\AA}^3) \quad \text{for Co-B} \quad (4)$$

$$\bar{V} = 11.42 - 1.52X \quad (\text{\AA}^3) \quad \text{for Co-P} \quad (5)$$

$$\bar{V} = 11.26 - 0.93X \quad (\text{\AA}^3) \quad \text{for Ni-P} \quad (6)$$

The values of  $\bar{V}_0$  of Co and Ni at the hypothetical pure state are  $11.42$  and  $11.26 \text{ \AA}^3$ , respectively. Thus the relative volume difference from the crystalline structure to the amorphous one is 1.6% for both Co and Ni. These experimental results, at least, suggest that the amorphous structure seems to be affected more or less by the crystalline structure of each element.

The mean atomic volume  $\bar{V}$  of ternary amorphous Fe-P-B and Co-Si-B alloys is given in Fig. 6 and expressed by the following equations for both alloy systems.

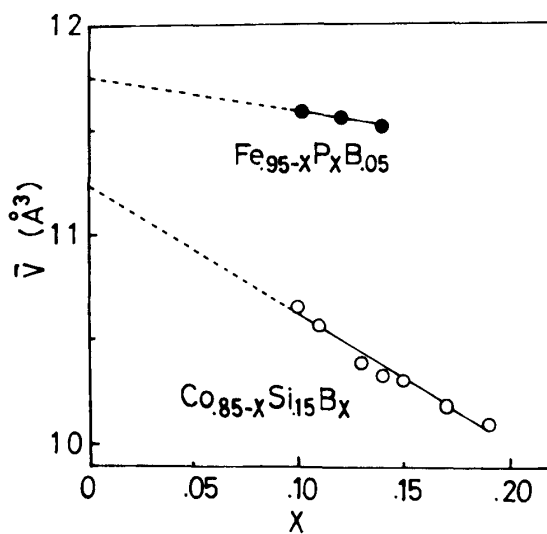


Fig. 6 Mean atomic volume of ternary amorphous alloys.



$$\bar{V} = 11.74 - 1.60X \quad (\text{Å}^3) \quad \text{for Fe-P-B} \quad (7)$$

$$\bar{V} = 11.23 - 6.20X \quad (\text{Å}^3) \quad \text{for Co-Si-B} \quad (8)$$

As shown in the figure, the  $\bar{V}_0$  in the limit where  $x \rightarrow 0$  gives the volume of hypothetical binary  $\text{Fe}_{95}\text{B}_5$  and  $\text{Co}_{85}\text{Si}_{15}$  amorphous alloys which can not be prepared by a melt quenching technique. The value of  $\bar{V}_0$  of  $\text{Fe}_{95}\text{B}_5$  amorphous alloy is in reasonable agreement with that of extrapolation in binary Fe-B amorphous alloys in Fig. 4. The value of  $\bar{V}_0$  of  $\text{Co}_{85}\text{Si}_{15}$  amorphous alloy is similar to  $\bar{V}$  of  $\text{Co}_{85}\text{P}_{15}$  and higher than  $\bar{V}$  of  $\text{Co}_{85}\text{B}_{15}$ .

Summarizing these results, the relative volume difference of each amorphous pure metal was estimated, using the extrapolation of the composition dependence in binary alloys, to be  $2.8 \pm 0.8\%$  which is larger than those of crystalline state. This relative volume difference may characterize the transition from the crystalline phase to amorphous one. The addition of B and P gives the gradient concentration dependence of volume for the hypothetical pure metal amorphous alloys by 6.8 and 1.3%, respectively, as shown in Figs. 4 and 5.

The packing density  $\eta$  given by the relation of  $\eta = \eta_c (\bar{V}'_0 / \bar{V}_0)$ , in where  $\eta_c$  is the packing density in the crystalline state such as 0.75 for f.c.c. or h.c.p. and 0.68 for b.c.c. structure. The present results give the packing density as follows; 0.66, 0.74 and 0.74 for Fe, Co and Ni, respectively. In our case, there is not an arbitrary assumption for the hard sphere volume of metalloid elements so as to use in the previous calculation<sup>18)</sup>. However, our values are apparently larger than those of the previous calculation<sup>18)</sup> and the so-called relaxed dense random packing (DRP) models<sup>19)</sup> also do not give this large value in the packing density.

Polk<sup>1)</sup> has suggested the following concept based on the previous experimental data and model calculations for several kinds of amorphous alloys; the basic feature of the atomic scale structure of amorphous alloys is mainly characterized by the DRP structure of transition metal atoms in which the metalloid atoms of relatively small size occupy the vacant spaces formed by the transition metal atoms and thus the local ordering unit becomes the  $\text{A}_3\text{B}$  or  $\text{A}_2\text{B}$  type similar to those in the corresponding crystal structures. It is then quite realistic that the contribution of local ordering units of  $\text{A}_3\text{B}$  or  $\text{A}_2\text{B}$  type to the DRP structure of metallic elements strongly depends upon the metalloid content. That is, the contribution of local ordering unit to the DRP structure of metallic elements is not so evident in lower metalloid content where the number of local ordering units is small, but the contribution becomes dominant over the DRP structure<sup>16)</sup>, increasing

the metalloid content.

The concentration dependence of densities observed in this work is probably related to the above concept; namely the contribution of local ordering units to the DRP structure of amorphous alloys depends on the metalloid concentration. The radial distribution function analysis with diffraction experiments must reveal about the structural features of amorphous alloys. One of the authors (Waseda) reported the radial distribution function data of Fe-P and Fe-B<sup>17)</sup>. The variation of the nearest neighbour distance  $r_1$  shows a similar concentration dependence observed in the density measurements. However, there are no data for other amorphous alloys presently investigated. But the first nearest neighbour distance  $r_1$ , which mainly corresponds to the distance of metal-metal atom, could be estimated from the position of the first maximum in the diffraction pattern using the following equation<sup>20)</sup>;

$$Q_1 \cdot r_1 \approx 8.0 \quad (9)$$

where  $Q_1$  is the position of the first maximum in the diffraction pattern in the unit of  $\text{\AA}^{-1}$ . This equation is a crude but useful approximation, because it was found to give the qualitative feature of the variation for the first nearest neighbour distance in some amorphous alloys<sup>14,15)</sup>. The concentration dependence of  $r_1$  for quaternary amorphous alloys presently investigated is given in Fig. 7. The  $r_1$  were calculated

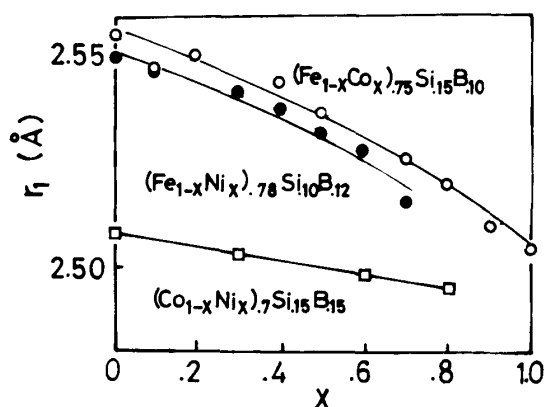


Fig. 7 First nearest neighbour distance of Fe-Ni, Fe-Co and Co-Ni amorphous alloys containing a fixed metalloid content.

from X-ray diffraction data of Mo-K $\alpha$  radiation. These results qualitatively support the discussion above mentioned. For example, as shown in Fig. 1, the slope of the concentration dependence of  $D$  in binary (Fe or Co)-B and Fe-P systems slightly changes near the composition range of 20 at% B and 18 at% P, respectively. A similar change of the slope is also found in the results of the first nearest neighbour distance  $r_1$  as given Ref. 17. The difference in the composition range where the change occurs may be related to the size factor difference between

metal and metalloid atoms. Namely metalloid atoms which have larger atomic radii gives a lower composition, thus the lower composition range was found in the case of Fe-P alloys compared with that of Fe-B alloys. As shown in Fig. 7, it is again found that the effect of replacing metallic elements on the concentration dependence of the first nearest neighbour distance  $r_1$  is not so evident compared with that of metalloid elements. For a detailed discussion, more information is required such as the radial distribution functions which are under investigation.

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