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COMMENT ON THE INTERPRETATION OF THE FIRST PEAK OF THE RDF OF AMORPHOUS METALS (*)

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Abstract. — The first peak of the RDF has been calculated for the dense random packed (DRP) and Ni₃P structures with a gaussian broadening of the atomic positions. It is found that the position of the broadened first peak of the RDF of DRP is 2 \% greater than the hard sphere diameter. The contributions of Ni-Ni and Ni-P pairs to the first peak of the RDF of amorphous Ni-P are discussed by comparing this peak to the calculated broadened peaks.

Introduction. — Structural models for amorphous metals which are currently most widely accepted are based on a dense random packing (DRP) of hard spheres. Bernal [1] first considered such structures in detail as a structural model for monatomic liquids; it was subsequently suggested [2-5] that such DRP structures could provide suitable models for amorphous monatomic solids — in particular, amorphous metals.

In considering such a model, the effective hard sphere diameter, \( D_{\text{eff}} \), of the atoms comprising the glass must be specified. This can be done by matching the experimental radial distribution function (RDF) to that for hard spheres. However, the determination of \( D_{\text{eff}} \) is complicated by experimental uncertainties and by the fact that amorphous metals generally are alloys containing elements which may differ in size and which do not interact identically to hard spheres.

Cargill [5] first compared in detail an amorphous metal RDF to that for a DRP structure. He matched the second through fifth peak maxima of the function \( \rho(r)/\rho_0 \) for amorphous Ni-P to that of Finney [6] for DRP and, noting that the Goldschmidt radii of Ni and P differ by only 3 \%, determined a \( D_{\text{eff}} \) of 2.42 Å, 3 \% less than the Goldschmidt radius of Ni.

Polk [7, 8] pointed out the possible importance of compositional short range order and atomic size differences in the structure of amorphous Pd-Si and Ni-P. He showed [8] that it was topologically possible to have a random packed structure that approximated the short range order of Pd₃Si and Ni₃P by considering, as a first order approximation of such a structure, the structure obtained by placing the Si or P in the larger voids inherent in a dense random packing of metal atoms. The Goldschmidt diameter of the metal atom was chosen as its \( D_{\text{eff}} \) while the metal-metalloid distances were proposed to be similar to those in the crystalline phases.

Cargill and Cochrane [9] have reported that a least squares fit of 4 \( \pi r [\rho(r) - \rho_0] \) of DRP and that of Ni₇₆P₂₄, excluding the region of the first peak, results in a \( D_{\text{eff}} \) of 2.46 Å while the first peak position \( (R_1) \), defined as the midpoint at 3/4 maximum) for Ni₇₆P₂₄ occurs at 2.56 Å. They suggest that the Ni-Ni separation is increased 3 \% from that of DRP with the Ni Goldschmidt radius, (2.49 Å) because of the introduction of P, while the higher \( r \) peaks suggest a lower \( D_{\text{eff}} \) since they are due to configurations containing both Ni-Ni and Ni-P distances.

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Dixmier and Duwez [10] observed small shoulders on the lower side of the first peak for Pd-Ni-P alloys and attributed these shoulders to the shortened metal-phosphorus distance. Such shoulders were also found for Co-P and Ni-P alloys [9]. The RDF of dense random packings of hard spheres of two different sizes have been investigated by Sadoc et al. [11].

In this paper, the first peak of the RDF has been calculated for the DRP structure of one sphere size and the Ni$_3$P structure with a gaussian broadening of the atomic positions. The DRP peak is compared to that for Ni$_3$P and amorphous Ni-P in order to determine the $D_{el}$ of Ni in these structures. Finally the separation of the Ni-P and Ni-Ni contributions to the first peak of amorphous Ni-P is discussed.

**Calculation of broadened peaks.** — The RDF used for DRP is that reported by Finney [6] in the form of a histogram for a hard sphere diameter of $D = 1.00$ and $AD = 0.02$. This was scaled to a $D$ of 2.50 Å to approximate the Ni diameter. The number of pairs given in Finney's data for 1.00 (i.e., contact) were all assigned the distance 2.50 on the revised scale, while the number of pairs for $1.00 < D \leq 1.02$ were distributed uniformly among the values 2.51, 2.52, 2.53, 2.54 and 2.55, etc. The first peak of the RDF for DRP with $D = 2.50$ is represented by the histogram of figure 1.

The function $r\rho(r)$ which undergoes gaussian broadening. Thus the function $r\rho(r)$ has been gaussian broadened and reconvered to the broadened $4\pi r^2 \rho(r)$ which is plotted as the curve in figure 1. The broadening was chosen so as to produce a peak height of $\sim 2\pi$, similar to those observed for amorphous metals.

For the broadened peak, $R_1$ (the midpoint at 3/4 maximum) is at 2.55 Å, i.e., 2% greater than the hard sphere diameter. This shift is due primarily to the asymmetric shape of the first peak of the DRP structure; broadening $r^2 \rho(r)$ instead of $r\rho(r)$ would provide almost as great a shift. The asymmetry of the original peak remains measurable; at half-maximum, the peak has a width of 0.21 Å to the left and 0.25 Å to the right of the $r$ of the peak's maximum.

Based on the data reported by Rundqvist et al. [12] for the Ni$_3$P structure, a broadened first peak of the RDF was calculated in the same manner for this structure. The Ni and P contributions were weighted by their respective atomic numbers. Figure 2 displays the total first peak as well as the separate contributions from Ni-Ni and Ni-P pairs. For the Ni-P peak, $R_1$ is 2.29 Å; for the Ni-Ni peak, $R_1$ is 2.68 Å. These $R_1$'s approximate the average Ni-Ni and Ni-P first neighbor distances since, in Ni$_3$P, the average Ni-P near neighbor distance is 2.28 Å; the average Ni-Ni distance (averaged over distances less than 3.10 Å) is 2.68 Å. The total first peak has a $R_1$ of 2.64 Å, $\sim 0.08$ Å more than the weighted average of the $R_1$'s of the Ni-P and Ni-Ni peaks.

![Fig. 1.](image1.png)  
**Fig. 1.** — Finney's RDF of DRP with $D_{el}$ 2.50 Å [6] plotted as the histogram. The curve is this RDF after a gaussian broadening of $4\pi r^2 \rho(r)$.

![Fig. 2.](image2.png)  
**Fig. 2.** — The first peak of the RDF of the Ni$_3$P structure [12] with the separate contributions of the Ni-P and Ni-Ni pairs also shown. Superimposed is the peak for DRP.
It is noted that the broadened Ni-Ni peak of Ni$_3$P has an asymmetry essentially the same as that obtained for the RDF of DRP. Further, the ratio of the average Ni-P distance to the average Ni-Ni distance is $2.28/2.68 = 0.85$. Thus subtracting half of the Ni-Ni average separation from the Ni-P average separation indicates that P has an effective diameter which is 70% of that of Ni. This suggests that the appropriate sphere sizes for a random packed structure of two sphere sizes to model amorphous Ni-P may be in the ratio of 0.70 to 1.00.

Figure 3 illustrates the calculated peak for a hypothetical crystalline structure of Ni$_{92}$P$_{18}$. The peak was calculated by assuming that the P atoms had the same environment as in Ni$_3$P, that the Ni-Ni first neighbor distances were the same as in Ni$_3$P, and that the number of near-neighbor pairs was the same in Ni$_3$P and Ni$_{92}$P$_{18}$. Thus the $R_1's$ of the Ni-P and Ni-Ni peaks remain the same while the Ni-Ni coordination increases both on an absolute scale and relative to the Ni-P peak.

**Discussion.** — The imposition of a gaussian broadening upon the RDF of DRP has been shown to result in a $R_1$ which is $\sim 2\%$ greater than $D_{\text{eff}}$. This broadened peak for $D_{\text{eff}} = 2.50$ Å is superimposed on the peak of Ni$_3$P in figure 2. Since the Ni-Ni peak of Ni$_3$P has a $R_1$ of 2.68 Å, $R_1$ of 2.55 for DRP, the $D_{\text{eff}}$ of Ni in Ni$_3$P is $\sim [2.50 + (2.68 - 2.55)] = 2.63$ Å.

Figure 4 shows the first peak for Ni$_{81.4}$P$_{18.6}$ [13] superimposed on the broadened first peak of DRP with $D_{\text{eff}} = 2.50$ Å which has been shifted by 0.02 Å to approximate the same peak for $D_{\text{eff}} = 2.52$ Å. This comparison suggests that $D_{\text{eff}}$ of Ni in amorphous Ni$_{81.4}$P$_{18.6}$ is $\sim 2.52$ Å, i.e. 1% greater than its Goldschmidt radius.

Similarly, $D_{\text{eff}}$ of Ni in Ni$_{72}$P$_{28}$ [13] can be shown to be $\sim 2.54$ Å. Since $D_{\text{eff}}$ of Ni in Ni$_3$P, a crystalline alloy of similar composition, is $\sim 2.63$ Å, the Ni $D_{\text{eff}}$ decreases $\sim 3.6\%$ upon becoming amorphous, for this composition, in spite of the presence of two different sphere sizes.

The difference of $\sim 2\%$ for $D_{\text{eff}}$ and $R_1$ of the broadened peak is important when considering the density of a proposed model since a 2% charge in $D_{\text{eff}}$ will produce an almost 6% charge in the calculated density.

Since both the Ni-Ni first peak in Ni$_3$P and the DRP first peak are markedly asymmetric, it is likely that the Ni-Ni contribution to the first peak of amorphous Ni-P will also be asymmetric. Thus subtracting a symmetric peak, obtained by reflecting the high $r$ section of the first peak about its maximum, from the full peak is not likely to produce a good estimate of the peak due to reduced Ni-P distances.

As has been suggested earlier [7, 8], it is proposed that the magnitude and distribution of near neighbor distances in amorphous Ni-P should be similar to that in Ni$_3$P. Thus the calculated peaks for Ni$_3$P and Ni$_{81.4}$P$_{18.6}$ should give an indication of the peak shapes expected for amorphous Ni-P where the experimental peak is a sum of the Ni-P and Ni-Ni peaks. This suggests that, as in figure 3, the Ni-P contribution...
would produce no obvious substructure in the first peak of low P alloys whereas, for high P alloys, a shoulder should appear as a departure from gaussian-like shape such as exhibited by the total curve of figure 2 at ~ 2.4 Å. This predicted behavior is different than reported for the more complicated, i.e. three sphere size, case of Pd-Ni-P [10]. There a distinct shoulder was obtained in \( W(r) \) for the 15 at % P alloy and the shoulder size did not increase with increasing P content. The shoulder on the first peak of the RDF of Co\(_{78}\)P\(_{22}\) [9] may appear too small because of the subtraction of a symmetric central peak. Cargill [14] has subsequently found that, for Ni-P alloys, a shoulder is found for high P alloys but not low P alloys when a symmetric central peak is subtracted from the first peak of \( W(r) = 4 \pi r [\rho(r) - \rho_0] \). Experimental uncertainties do, of course, make this separation very difficult.

Figures 2 and 3 show that, with the same distribution of Ni-P and Ni-Ni distances, the height of the first peak of the RDF will decrease in height with increasing P content. Such a first-peak broadening has been reported [10, 13] and this change in the ratio of the two subpeaks can account for most of the broadening.

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