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ELECTRON DIFFRACTION STUDY OF THE LOCAL ATOMIC ARRANGEMENT IN THIN FILMS OF AMORPHOUS GALLIUM, IRON AND NICKEL

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Résumé. — Nous avons préparé des films minces de gallium, de fer ou de nickel amorphes par condensation à basse température dans un vide poussé, et nous avons étudié la diffraction d'électrons transmis par ces films. L'analyse de la distribution radiale du spectre formé de halos diffus permet d'examiner l'arrangement atomique local dans le gallium, le fer et le nickel amorphes. La valeur expérimentale de $W(r)$ ($= S(r) S_0$), comparée à sa valeur calculée à partir de plusieurs modèles de structure, nous indique que la structure du gallium amorphe est très proche de celle du β -gallium très désordonné, et que celles du fer ou du nickel amorphes sont représentées à une bonne approximation par un assemblage compact désordonné.

Abstract. — Thin films of amorphous gallium, iron and nickel have been prepared by low temperature condensation in high vacuum, and a transmission electron diffraction study of these films has been undertaken. The radial distribution analysis of the patterns composed of diffuse halos has been carried out in order to investigate the local atomic arrangement in amorphous gallium, iron and nickel. $W(r)$ ($= \rho(r)/\rho_0$) experimentally derived has been compared with $W(r)$'s calculated from several structural models, leading to the conclusions that the structure of amorphous gallium is considerably similar to that of highly disordered β -gallium and that the structures of amorphous iron and nickel are, to a good approximation, represented by a dense random packed structure.

1. Introduction. — It is an interesting problem to study physical properties of disordered structure without long range order in atomic arrangement such as an amorphous state. Unfortunately, very few elements become amorphous in bulk. However, many elemental amorphous materials are obtained by means of condensation on to cold substrate, though they are in a state of thin film. Knowledge about the local atomic arrangements in the films is, however, very poor and plausible pictures of the structures are not yet found. It is the present purpose to clarify the local atomic arrangements in amorphous gallium, iron and nickel films prepared by low temperature condensation by means of the radial distribution analysis of diffuse electron diffraction patterns.

2. Experimental. — Gallium of 99.999 % purity and iron and nickel both of 99.99 % purity were evaporated from a tungsten helical filament, and were condensed on substrate of Polyvinyl Formvar film at liquid helium temperature (LHeT) in a vacuum $< 1 \times 10^{-6}$ torr for gallium and $< 5 \times 10^{-6}$ torr for iron and nickel in diffraction apparatus equipped with a rotating sector [1]. The thicknesses of the gallium, iron and nickel films were roughly estimated from evaporated quantities to be about 150, 90 and 20 Å, respectively. The procedures for photographing

of electron diffraction pattern, determination of s -value ($= 4 \pi \sin \theta / \lambda$, where 2θ is the scattering angle and λ the electron wave length) and photometry were the same as described in a previous paper [2].

Thin films of gallium, iron and nickel condensed on substrate at LHeT showed diffraction patterns composed of very diffuse halos which were characteristic of highly disordered structure. The diffuse pattern of gallium changed to a ring pattern of β -gallium and afterwards to a diffuse pattern of liquid gallium on heating. The diffuse halo patterns of iron and nickel changed to ring ones of bcc and fcc structures, respectively, on heating.

3. Radial distribution analysis. — As is well known, the radial distribution function (RDF) of monatomic amorphous solid is determined by numerically computing the following integral :

$$4 \pi r^2 \rho(r) = 4 \pi r^2 \rho_0 + \frac{2 r}{\pi} \int_0^{s_{\max}} s \cdot I_m(s) \exp(-Bs^2) \sin(sr) ds,$$

where $\rho(r)$ is the atomic density at a distance r from an atom, ρ_0 the mean atomic density, $I_m(s)$ the structure-sensitive intensity, s_{\max} the maximum value of s below which $I_m(s)$ is experimentally derived, and B a damping

factor which reduces ghost ripples due to the termination of $I_m(s)$ and is usually chosen so that

$$\exp(-Bs_{\max}^2) = 0.1.$$

The methods of derivation of the structure-sensitive intensity $I_m(s)$ from diffuse halo patterns and of removal of the contribution from substrate were the same as described in the previous paper [2].

Values of $I_m(s)$ were derived from the diffuse halo patterns in the range from $s = 1.8$ to 21.5 \AA^{-1} for gallium, in the range from $s = 2.3$ to 20.0 \AA^{-1} for iron and in the range from $s = 2.3$ to 19.5 \AA^{-1} for nickel, respectively. Those in the range from $s = 0$ to 1.8 \AA^{-1} for gallium, and in the range from $s = 0$ to 2.3 \AA^{-1} for iron and nickel were extrapolated so as to smoothly reach -1.0 at $s = 0$. As the mean densities of the present films were not measured, the values of crystalline α -gallium, bcc iron and fcc nickel were used as ρ_0 for the gallium, iron and nickel films, respectively. Since the feature of the experimental $W(r)$ ($= \rho(r)/\rho_0$) is relatively insensitive to error in value of the mean density and neglect of the intensity of small-angle-scattering, the atomic arrangement in the film is discussed from the experimental $W(r)$.

4. Discussion on the local atomic arrangement in the gallium film. — As shown by curve a in figure 1, the peaks other than the well-resolved first one at 2.79 \AA are very broad in the $W(r)$ determined for gallium, and none is seen in a region of r beyond 12 \AA , which may indicate that order in the atomic arrange-

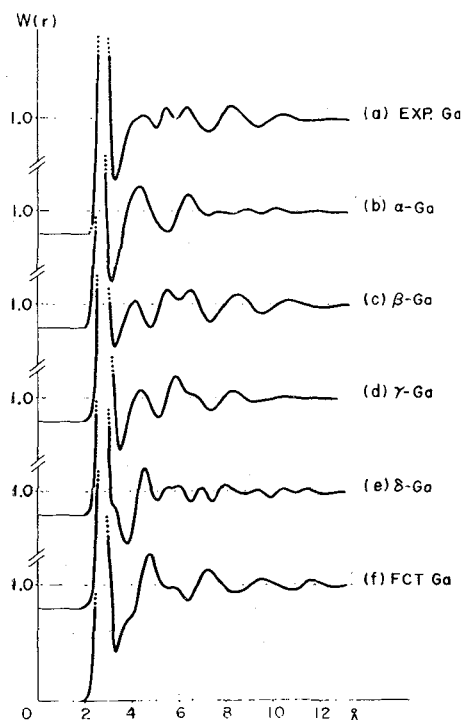


FIG. 1. — Curves a, b, c, d, e and f represent the experimental $W(r)$ for the gallium film and the $W(r)$'s calculated from models of disordered α -, β -, γ -, δ - and fct Ga structures, respectively.

ment in the film is very short-range and not so definite even within the above region. $W(r)$'s were calculated from disordered structural models with the same local atomic arrangements as those in α -[3], β -[4], γ -[5], δ -[6] and fct Ga [7], assuming Gaussian broadening of each radial shell to account for disordering displacement, and compared with the experimental $W(r)$ as shown in figure 1. The comparison shows that a general feature of the experimental $W(r)$ is satisfac-

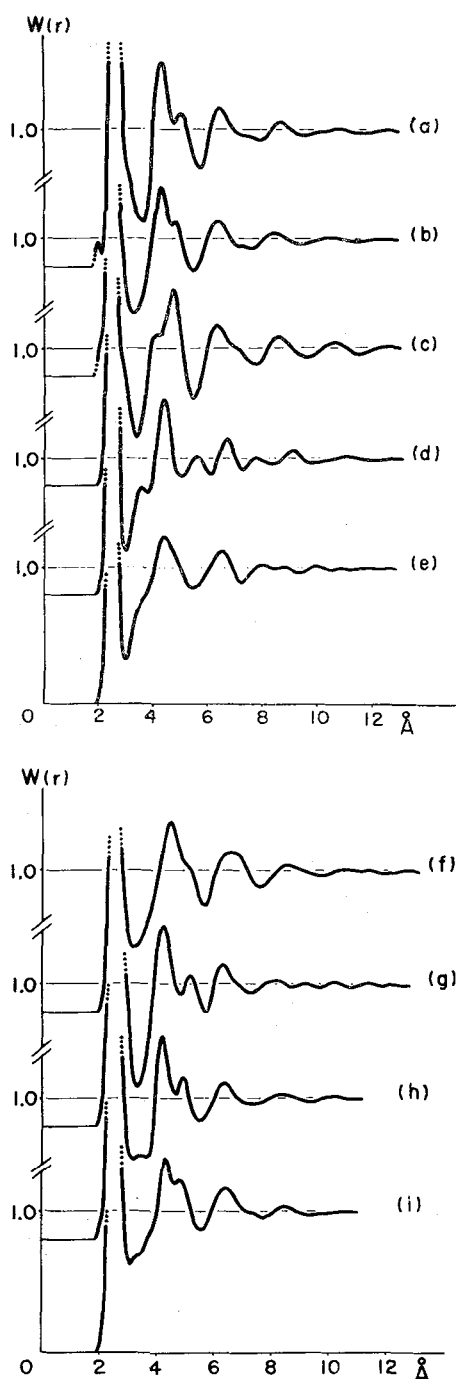


FIG. 2. — Curves a, b, c, d, e, f, g, h and i represent the experimental $W(r)$'s for the iron and nickel films and the $W(r)$'s calculated from models of disordered bcc, fcc, hcp, bct, A-15 and two dense random packed structures, respectively.

torily explained by the $W(r)$ of disordered β -Ga model rather than those of the other models, for peaks corresponding to those in the experimental $W(r)$ curve, especially to those at 5.5 and 6.3 Å, are seen only in the $W(r)$ of disordered β -Ga model, though positions of the corresponding peaks are slightly shifted. Such a question arises that the gallium film might be assemblage of minute β -Ga crystals. However, in the adopted β -Ga model radial shells due to the neighbors farther than the first neighbor suffer very large Gaussian broadening to be unexpected in crystal. Moreover, when the transition from amorphous Ga to β -Ga occurs, a rapid release of heat which amounts to more than half of heat of fusion, and a rapid change of electric resistivity characteristic of phase change are observed [8]. Therefore, it may be reasonable to conclude that the gallium film is in an amorphous state having the local atomic arrangement similar to that in highly disordered β -Ga, that is, many atoms have the same geometrical relation with nearest neighbors as that in β -Ga but the relation with farther neighbors is much disturbed.

5. Discussion on the local atomic arrangement in the iron and nickel films. — Curves a and b in figure 2 represent $W(r)$'s for the iron and nickel films, respectively. Features of the two curves, especially well-resolved first maxima and second maxima splitting into two peaks, are strikingly similar to each other. The features are seen also in the $W(r)$ for amorphous metallic alloys such as FePC [9] and NiP [10]. Positions of the first peaks for the iron and nickel films equal the nearest neighbor distances, 2.54 and 2.48 Å, of fcc iron and fcc nickel, respectively.

Iron has several polymorphisms such as bcc, fcc and hcp structures. Nickel has only a fcc structure. Disordered structural models were considered from bcc, fcc and hcp structures as in section 4, in order to clarify the local atomic arrangement in the iron and nickel films. Besides, two structural models were considered. One is a bct structure, because this structure is found in the martensite of iron. The other is A-15 structure, so-called β -tungsten one. This structure is not found in iron but exists in a thin film of chromium having bcc structure in bulk [11]. Curves in figure 2 represent $W(r)$'s calculated from the structural models. General shapes of the experimental $W(r)$'s for the iron and nickel films are considerably

similar to that of the $W(r)$ for disordered A-15 structure, but the similarity is unsatisfactory, because there are differences in position of peak, especially of the subsidiary peak on the right side of the second maxima.

A structure that metalloid atoms enter holes of a dense random packed structure constructed by metal atoms is considered as a plausible structural model for some amorphous metallic alloys [12]. A structure which resembles the dense random packed structure is generated by a computer calculation in which hard spheres of the same size are successively added to a small initial nucleus so that each added sphere may take at each step the position of three-fold contact with the surface spheres [13]. The dense random packed structure composed of various numbers of atoms were constructed in a computer, triangle, tetrahedron, dodecahedron or icosahedron composed of 3, 4, 7 or 13 atoms, respectively, being chosen as the initial nucleus, and $W(r)$ curves were calculated from the structures. The two curves h and i in figure 2 represent $W(r)$'s for the cluster composed of 190 atoms with a triangle as an initial nucleus for iron and of 71 atoms with an icosahedron as an initial nucleus for nickel, respectively. The strong-weak nature of the second maxima in the experimental $W(r)$'s is distinctly seen in both of curves h and i, and, moreover, general shapes and peak positions of the curves are strikingly like those of the experimental $W(r)$'s for the iron and nickel films, respectively. Curves having a similar shape to that of curve h were derived, even if a tetrahedron, a dodecahedron or an icosahedron was used as an initial nucleus instead of a triangle for iron, so long as the number of atoms involved in the cluster is sufficiently large, e. g. 190 or more. Hence, the structure in the amorphous iron films may substantially be represented by the dense random packed structure. On the other hand, a nucleus of icosahedron seems to play an important role in the formation of the amorphous nickel film because a curve with the same feature as that of curve i was obtained only when an icosahedron was chosen as an initial nucleus and the number of atoms in the cluster was 71 or so. To sum up, it is concluded that the structure in amorphous iron and nickel films condensed on substrate at LHeT is not an assemblage of minute crystals of bcc or fcc structure but that of clusters represented by the dense random packed structure.

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