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MÖSSBAUER SPECTROSCOPY OF AMORPHOUS ALLOYS

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ABSTRACT

Electronic and atomic structures of ferromagnetic amorphous alloys containing iron as a major component are studied by means of Mössbauer spectroscopy. In accordance with many experimental results, which indicate that short range ordering in the atomic arrangements are considerably developed in the amorphous structure, the Mössbauer spectra of the amorphous alloys can be analyzed with the assumption that the near neighbour configurations are almost the same as those in the crystalline state. Comparing with the ordinary crystalline alloy structures, no essential difference or strangeness in the internal field distribution, isomer shift, quadrupole effect, and defect structures are found, differing from the generally accepted concept of simple random dense packing structure.

INTRODUCTION

One of the most popular and generally accepted concepts on the atomic arrangement in the amorphous structure of metals is the random dense packing of atoms, which was first proposed by Bernal (1). In Fig. 1 is shown a random dense packing model by Bernal, in which the coordination number varies between, say, 7 and 13. He treated it statistically and exhibited the distribution of the number of first neighbours, as shown in Fig. 2. In such a distribution, the majority is not always 12, only which appears in the crystalline closest packing structures, but a large number of deviations with odd coordination numbers, 7, 8, 9, 10, 11 and 13, appear, being associated with defect lattice structures.

Since the crystalline field in the amorphous structure is perturbed mainly by the dificit in the coordination number and thereby introduced asymmetrical neighbouring configuration and possibly diffused holes in the defect structure, the Mössbauer spectroscopy, which gives information on the short range interactions, such as chemical bonding, between near neighbour atoms, looks useful to elucidate the electronic structure and defects in atomic ordering in the amorphous structure. Amorphous alloys containing a ferromagnetic element, especially iron, as the major component were found

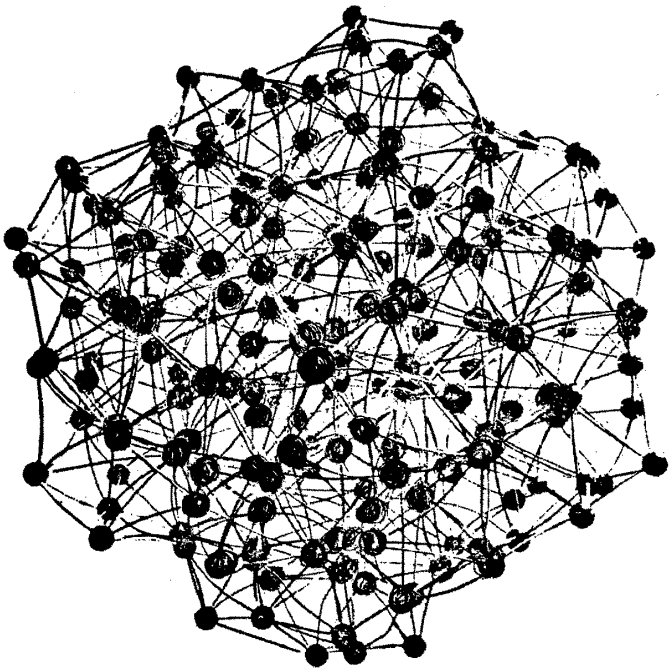

Fig.1. A random dense packing model made by balls and spokes by Bernal (1)

to be ferromagnetic, and, therefore, their Mössbauer spectra usually exhibit broad six peak patterns which are useful for the spectral analysis to find various components corresponding to various atomic configurations in the stracture. The information thus obtained from the Mössbauer spectroscopy is expected to directly connect with the proposed structural models for random dense packing. Nevertheless, the degree of randomness in the atomic arrangements in the amorphous alloys is not always clarifies and well defined, as is briefly mentioned in the following.

The random lattice structure of the amorphous alloys has been concluded from the high electrical resistivity, its small temperature coefficient, and very broad X-ray diffraction pattern, which are respectively comparable to those of liquid metals. Actually, the Bernal model was first proposed to interpret the liquid structure, but later it turned out that the model was rather suitable to explain the amorphous structure than the liquid structure.

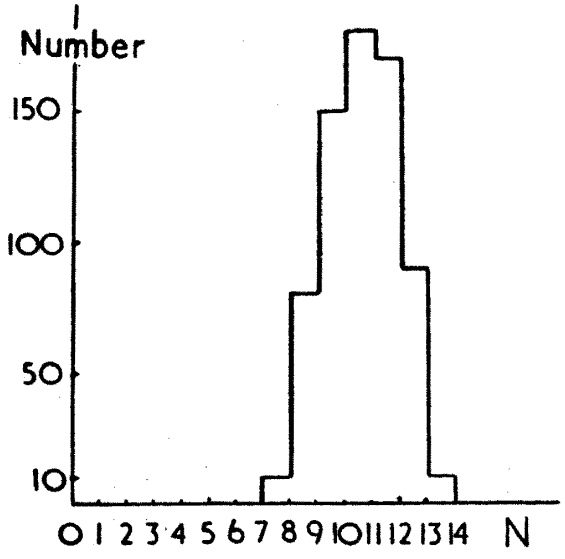

Fig.2. A histogram by Bernal showing a distribution of the coordination numbers in a random dense packing model.

This is because the Bernal model can give the splitting in the second peak of the two body corelation function in the random distribution of atoms, which is always obtained from the halo diffraction patterns from amorphous alloys, but not from the melt. This means that the amorphous alloys have a degree of order higher than that of the molten metals. There exist some more implications for much higher degree of ordering in the amorphous state than what would be expected from the Bernal model. For instance, Doi (2) carefully analyzed the breadth of the first corelation peak by taking consideration of linear atomic arrangements in the structure, and concluded that atoms are arranged in lines for five atomic distance or so and, therefore, the amorphous structure could be regarded as the aggregates of very small crystallites. Many physical properties and characteristics of the amorphous alloys also reflect the crystalline nature (3).

The random dense packing models including that by Bernal have suffered various examinations and improvements primarily so as to fit the results of X-ray diffraction studies: Bennett (4) first constructed by computer a random dense packing of spheres, but could not reproduce the second maximum split in the distribution corelation. Sadoc et al. (5) used a mixture of spheres with two different sizes in the packing computation and exhibited the second maximum split, while Ichikawa (6) employed the spheres of a unique size and certain restriction rule in packing manner and successfully reproduced the second maximum split. On the other hand, Doyama (7) has recently realized that when an interatomic potential was given and atomic relaxations were allowed in the computer constructed random dense packing structure, the second maximum split reappeared.

Such an intricate situation in the studies of the amorphous structure as above mentioned leads us to the conclusion that the degree of ordering in the atomic arrangements in the amorphous alloys is undoubtedly higher than that expected from ordinary random dense packing models but the extent of ordering and the corresponding real structure are not known.

Tsuei et al. (8) were the first to measure the ^{57}Fe Mössbauer spectrum of Fe-P-C amorphous alloy. They obtained a broad ferromegnetic six line pattern very similar to that obtained by the present study, which is shown in Fig. 3, and analyzed it with the assumption that each iron atom has seven nearest neighbours in the structure and the pattern consists of five main spectral components. However, the selected number of nearest neighbours was not justifiable (9) and the five decomposed spectral components were not identified each since no special relationship, such as the binomial distribution law, existed among their analyzed relative intensities. Later, they analyzed a similar amorphous pattern of an Fe-P-C alloy not using the near neighbour configurations and their distribution but by a Fourier transform method, and obtained an internal field distribution curve, as shown by a dotted line in Fig. 4. The curve shows a wide spread distribution including the zero and near-zero field components. They attributed the weak field components to the random lattice disturbance reducing the magnetic moments of a large part of the constituent iron atoms. Their result is quite different from the present author's curves, small circles and full line in Fig. 4 for $Fe_{80}P_{17}C_3$ alloy and full line in Fig. 7 for $Fe_{83}B_{17}$ alloy. The difference has arisen from that they did not evaluate the non-uniform orientation distribution of spins and simply assumed the peak ratio as 3 : 2 : 1 : 1: 2 : 3. Too much emphasis seems to have been placed on the defective structures in the former studies of the amorphous alloys including the above one. It should be noted that the amophous iron alloys usually contain large amounts of metalloid atoms, which strongly interact with iron atoms in the solid solution state and change the electronic structure of iron, especially the 3d

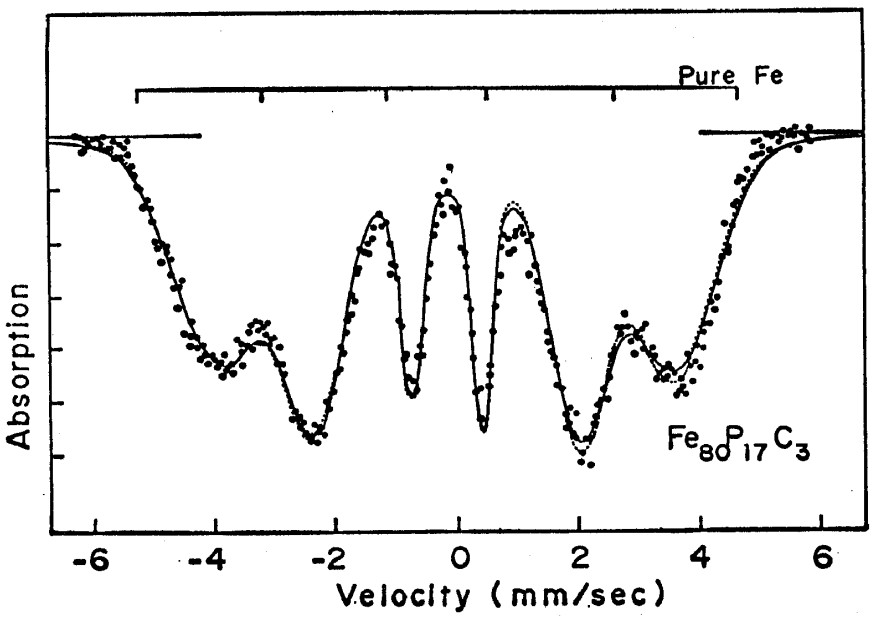

Fig.3. A Mössbauer spectrum of $Fe_{80}P_{17}C_3$ amorphous alloy mad by rapid cooling from the melt. Full line is calculated with the assumption of BCC near neighbour configuration and dotted line the FCC configuration.

configuration. Therefore, before discussing the effect of defective structures on the appearances of Mössbauer patterns and the changes in the Mössbauer parameters such as the internal field reductions, the alloying effect must be first taken into consideration. Another interesting example

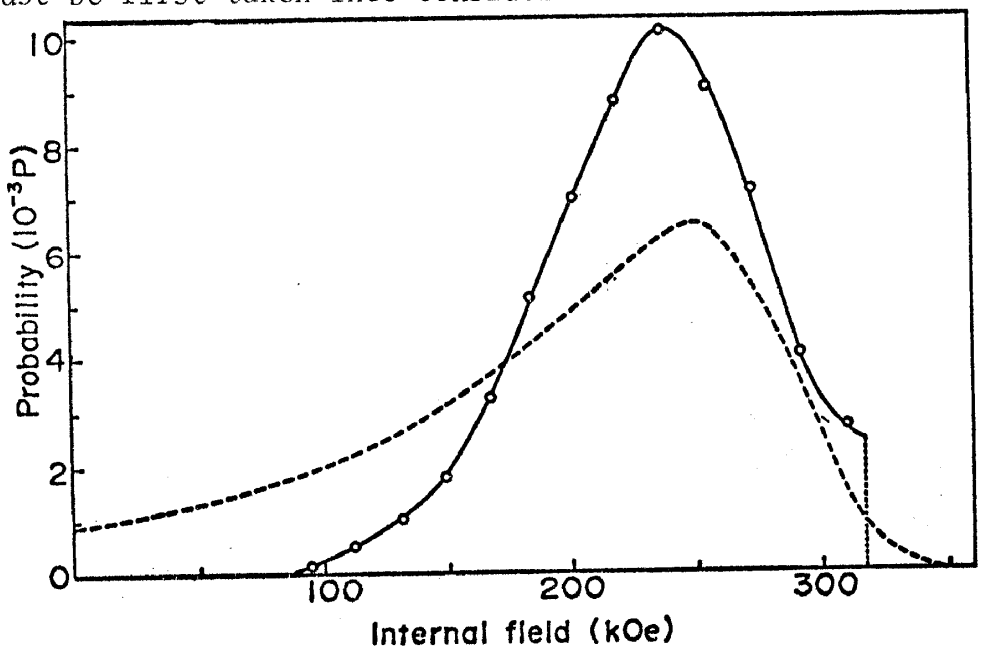

Fig.4. Calculated internal field distribution curves for Fe-P-C amorphous alloys; dotted line is by Tsuei et al. (8) for $Fe_{75}P_{15}C_{10}$, and circles and full line by the present author (10) for $Fe_{80}P_{17}C_3$.

of the analyses of Mössbauer spectra of ferromagnetic amorphous alloys has been given by Gonser et al. (11). They attempted to analyze the Mössbauer pattern of an amorphous Fe-B alloy by assuming the coordination deficiencies based upon the Bernal model. That is, they employed the coordination number distribution shown in Fig. 1, with the second assumption that the reduction

of internal field of iron was proportional to the dificit in coodination number from the full number, 12. Their calculaiton fairly fit the experimental data, but this result cannot be fully justified too, because the alloying effect is totally not taken into account in their analysis. It must be worthy to show herewith in Fig. 5 the Mössbauer spectra of three different alloys with more or less the same iron concentrations and the uniform solution states. Note that the patterns look quite the same even though the above two are of the amorphous alloys and the third one is of an crystalline solid solution alloy. This means that the appearance of the Mössbauer patterns of amorphous alloys shown in Fig. 3 (and in Fig. 5(a) and (b)) is not characteristic of the amorphous structure but mostly rising from the solution alloying effect.

RESULT AND DISCUSSION

Thin ribbons of amorphous $Fe_{80}P_{13}C_7$, $Fe_{80}P_{13}C$, and $Fe_{83\sim88}B_{17\sim12}$ alloys with the dimensions of 1~5 mm x 0.03 mm x 2000~5000 mm were produced by ejecting the molten alloys from a narrow nozzle onto a fast rotating disc (10). For Mössbauer spectroscopy, the ribbon was cut into pieces and an area of 20 mm square was made by putting them side by side without gaps. The thickness of 0.03 mm was suitable for γ-ray transmission from a 30 mCi ^{57}Co source so that no chemical or mechanical treatment on the specimens were needed. Most of the measurements were carried out at room temperature, where the alloys were stable and magnetically achieved the local saturation. In the analysis of the broad Mössbauer patterns, attensions were paid to avoid ambiguities in obtaining the Mössbauer parameters of the spectral components; only the least number of reasonable assumptions were used in the computer fitting, as will be mentioned. To find the internal field distribution another method of analysis, the Fourier transform method, was also employed, in which no special mistakable assumptions were necessary.

A typical broad six line Mössbauer spectrum taken at room temperature is shown in Fig. 3. The average hyperfine field is about 80% that of pure iron, and the largest component seems to be as large as that, as the pure iron scale in the figure indicates. The ratio of the integrated intensities of the six peaks is 3 : 3.3 : 1 : 1 : 3.3 : 3, which shows that the electron spins and thereby the magnetic moments are considerably polarized in the direction of the film face. The polarization is more evident in the case of $Fe_{83}B_{17}$ alloy, which is shown in the middle of Fig. 5. When the Fe-P-C specimen was heated up to 200°C, the room temperature spectrum produced no changes, but when heated to 380°C, which is about 50 degrees below the amorphous-crystalline transision temperature, the integrated intensity ratio changed from 3 : 3.3 : 1 to nearly 3 : 2 : 1 while the shape of each peak remained unchanged, as shown in Fig. 6 (12). On heating to 430°C, the spectrum begins to decompose to more than three sets of six line patterns, among which the outermost sharp one exhibits a hyperfine field equal to that of pure iron. It is clear that long range atomic migrations occur at around this temperature and, therefore, the phase separation takes place. By resolving the spectrum into components and fitting is concluded that the stable phases, α-iron, Fe_3P, and Fe_3C appear at this stage. 560°C annealing increases the intensities of these stable phases. It is noteworthy that in the case of Fe-B amorphous alloys annealing below the transition temperature yields the spectral component of Fe_3B as an intermediate structure, which does not exist in the equilibrium phase diagram of this alloy system, and more stable phase, Fe_2B, before detected by X-ray diffraction. This means that very small Fe_2B clusters appear as an incipient crystallization stage (1). More strange phenomenon is that, when a vacuum deposited thin

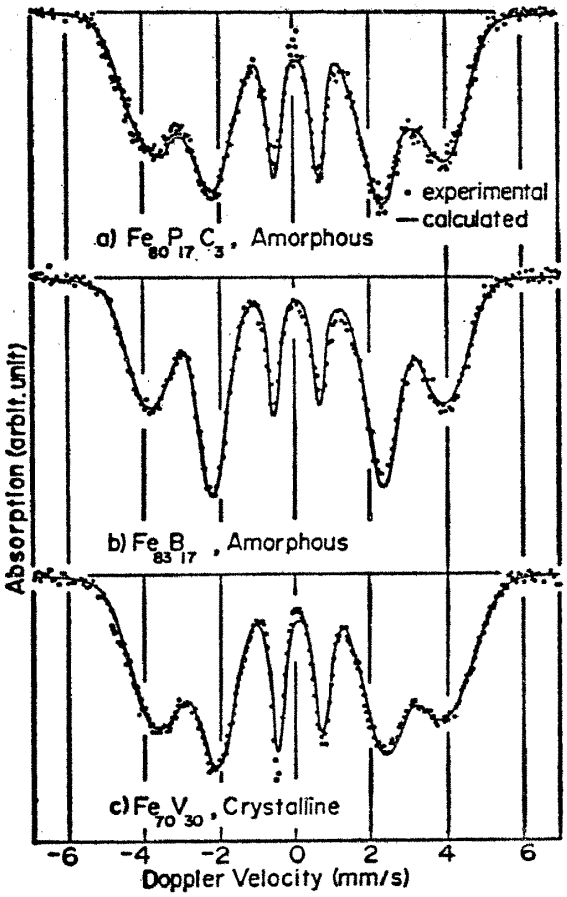

Fig.5 Mössbauer spectra of amorphous $Fe_{80}P_{17}C_3$, amorphous $Fe_{83}B_{17}$, and $Fe_{70}V_{30}$ alloy. Note that the three patterns look very similar but the last one is of a crystalline solid solution.

amorphous film of $Fe_{50}Si_{50}$ alloy is examined by the conversion electron reflection method, broad six line pattern similar to those in Fig.5 exhibits from the begining a certain fine structure which could be separated into at least three components. The above facts suggest that the structures of actual amorphous alloys are not always represented by an ideal random dense packing model but have intrinsic chemical interacitons giving rise to the strong alloying effect and/or tendency of molecule or cluster formaiton. Changes in the magnetization directions and structures of amorphous alloys are more precisely studied by various isochronal and isothermal annealings, and the above conclusions are verified.

Another interesting phenomenon concering the magnetization axes in the film is the effect of the earth magnetism on the peak ratio. When the direction of alignment of the Mössbauer apparatus is changed from that parallel to that perpendicular to the horizontal component of the earth magnetism, a considerable change in the peak ratio appears showing that about 4% of the magnetic moments in the Fe-P-C film are not stabilized but readily follow the direction of the earth magnetism. The easy axes of magnetization are not defined in the amorphous alloys, and, accordingly, unstable magnetic spins extremely capable of flipping are conceivable presumably associated with defective structures. Very soft ferromagnetic hysteresis and Kondo effect like resistivity minimum frequently observed in amorphous alloys are readily explained by such characteristic unstable moments.

In the analysis of the Mössbauer spectra, two mehtods are employed as before mentioned. In the Fourier analysis, no special neighbouring con-

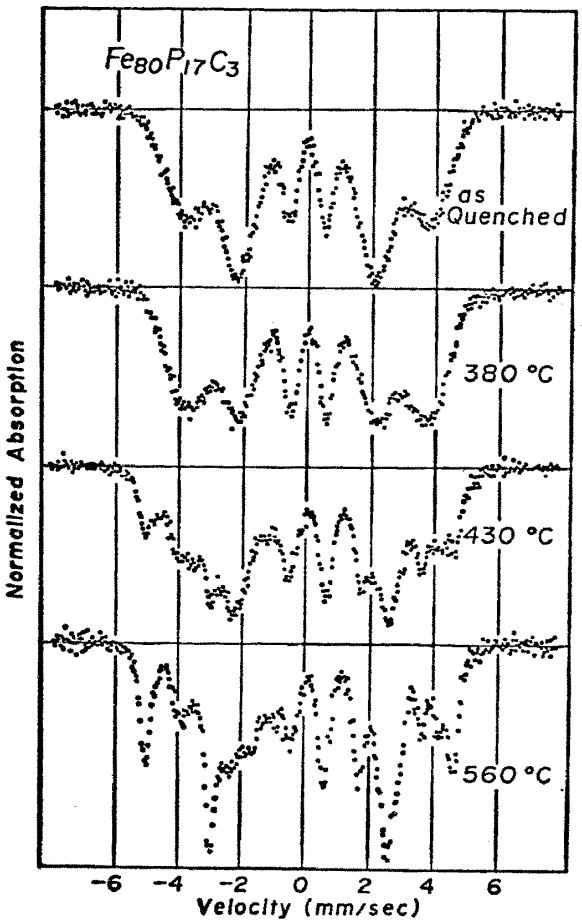

Fig.6 Room temperature spectra of amorphous $Fe_{80}P_{17}C_3$ alloy isochronally annealed at the temperatures indicated.

figurations for Mössbauer atoms are assumed but only the distribution of six line Lorentzians with various spreads, that is the distribution of the internal field components, is seeked for. One example of the Fourier analysis for amorphous Fe-B alloy is given in Fig.7 (12). The curve resembles the full line curve in Fig.4, which is obtained by the other method, and no weak field components like those in the dotted line analytical curve exist. In the other method, which take the near neighbour configurations into account, some basic assumptions are necessary; for instance, in accordance with the well developed atomic ordering in the amorphous structure and the value of the largest internal field component close to that of pure iron, the first and the second neighbour configuration for the probe iron atoms are assumed to be the same as those in the normal BCC structure. Other necessary assumptions are: Taking account of the distortion in the near neighbour atomic arrangements, especially of the farther neighbours than the first and the second, the half width of the Lorentzian assumed for all the components is taken as 20% wider than the observed value for pure iron. Metalloid atoms, P, C, B or any other in the amorphous structure, are tentatively assumed to occupy the near neighbour lattice positions substitutionally. Their distirbution is considered as completely random so that the binomial distirbution equaitons are simply employed to calculate the near neighbour configurations of the probe iron atoms. It is further assumed that the hyperfine field of the iron atoms is linearly reduced with the increasing number of eigher the first and the second neighbour foreign atoms. Another assumption is the isomer shift distirbution also linear to the number of the near neighbour atoms. In the case of Fe-P-C alloys, no distinction is given between the two kinds of the foreign atoms for the

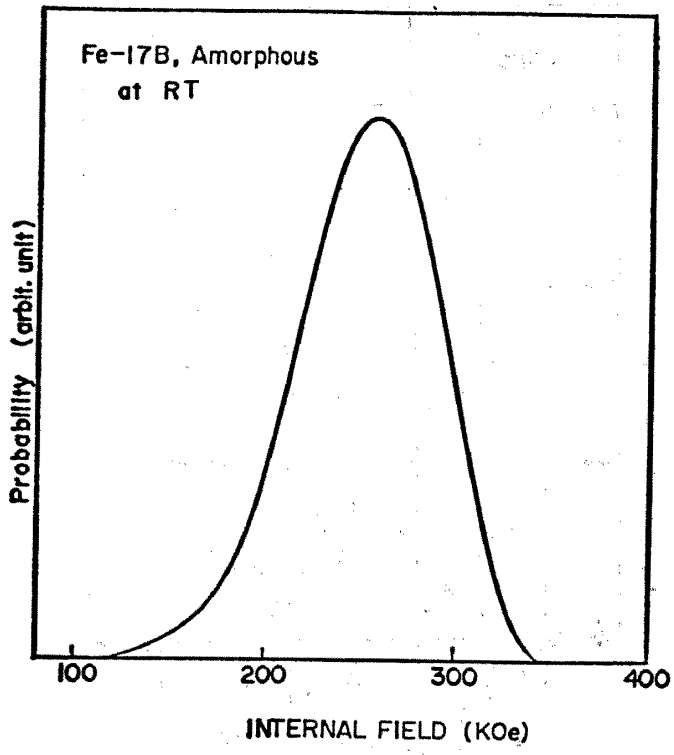

Fig. 7. The internal field distribution curve for Fe-17%B amorphous alloy calculated by the Fourier analysis.

amount of the reduction in hyperfine field and in isomer shift change by one foreign neighbour atom. Under these assumptions, the spectrum is synthesized by superposing many six line components and compared with the observed pattern to have the best fit.

Very good agreement between the above calculation and the experiment seen in Fig. 3 strongly supports that it is not required to assume any special basic structure with a peculiar near neighbour configuration for the amorphous state as other investigators have tried. For instance, to take consideration of defect structures, such as the seven neighbour configuration or a distribution of deficit numbers of neighbours according to the Bernal model like that in Fig. 2, is not justifiable at the present stage of the Mössbauer spectroscopy, since the spectrum is not specially characteristic of the amorphous structure but can be analyzed mainly in terms of the alloying effect. It would be worthy of note that the amount of reduction of the internal field by one neighbouring metalloid atom calculated for the amorphous structure is quite the same as those in the crystalline solid solutions so that the introduction of the defect structure into the spectrum analysis is not always necessary unless these parameters are more precisely examined by further experiments and calculations. On the other hand, the present author's method of analysis, which assumes a pseudo-crystalline state, has certain difficulty in it too. For instance, when a FCC type near neighbour configuration is assumed, a similar calculation is possible and the result is very similar, almost undistinguishable with the BCC type analysis, as shown by the dotted line in Fig.3. Although the FCC type analysis is not acceptable since FCC iron is not ferromagnetic, more careful examination seems to be required to distiguish the basic pseudo-crystalline structures in the analysis.

Many other interesting things are found by the Mössbauer spectroscopy of amorphous alloys and the experiments are still proceeding.

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