A STUDY OF LOCAL ATOMIC AND ELECTRONIC STRUCTURES OF LIQUID-QUENCHED La-Au ALLOYS BY 197Au AND 57Fe SPECTROSCOPY

S. Nanao, J. Sugiura, H. Ino, Y. Maeda, H. Sakai

To cite this version:

HAL Id: jpa-00218640
https://hal.archives-ouvertes.fr/jpa-00218640
Submitted on 1 Jan 1979

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
A STUDY OF LOCAL ATOMIC AND ELECTRONIC STRUCTURES OF LIQUID-QUENCHED La-Au ALLOYS BY $^{197}$Au AND $^{57}$Fe SPECTROSCOPY

S. Nanao, J. Sugiura, H. Ino, Y. Maeda* and H. Sakai*

Institute of Industrial Science, University of Tokyo, Roppongi, Minatoku, Tokyo 106, Japan

*Research Reactor Institute, Kyoto University, Kusumoto, Oka-a 580-04, Japan

Résumé.-Des alliages La-Au obtenus par trempe à partir de l'état liquide ont été étudiés par spectrométrie Mössbauer de $^{197}$Au et $^{57}$Fe. Les structures de la phase amorphe et de la phase B sur-saturée sont discutées. La température de Débyé du composé La$_{78}$Au$_{22.5}$Fe$_{0.5}$, amorphe et cristallin, est estimée à partir de la fraction d'effet sans recul de $^{197}$Au à 123K et 130K.

Abstract.- Mössbauer spectra of $^{197}$Au and $^{57}$Fe nuclei in the liquid-quenched La-Au alloys were measured, with which the atomic structures of the amorphous phase and the supersaturated B-La phase were discussed. The Debye temperatures for the amorphous and crystalline La$_{78}$Au$_{22.5}$Fe$_{0.5}$ specimens were estimated from the recoilless fraction of $^{197}$Au to be 123 K and 130 K, respectively.

1. Introduction.- La-Au alloy forms the amorphous phase in the vicinity of 20 at.%Au with liquid-quenching /1/. On the other hand, the dilute Au atoms in the La matrix have been observed to diffuse extraordinarily fast /2/, which suggests that at least a part of the Au atoms are expected to occupy interstitial-type lattice sites.

In the present paper, the structures of the amorphous and supersaturated La-Au alloys obtained by liquid-quenching were analysed from the position of Au atoms by Mössbauer effect of $^{197}$Au and $^{57}$Fe.

2. Experimental.- La-Au (2.8 ~ 22 at.%Au) and La-Au-Fe (18 ~ 25 at.%Au, 0.5 ~ 1 at.%Fe) alloys were splat-quenched in vacuo better than 2x10$^{-5}$ torr with the two-piston technique. The shape of the specimens was a disc about 20 mm in diameter and 50μm in thickness. Mössbauer spectra of $^{197}$Au and $^{57}$Fe were measured for them at 18 K and 77 K, respectively.

3. Results and Discussion.- The Mössbauer spectra of $^{197}$Au for the amorphous and crystallized (annealed at 350°C for 3 h.) La$_{78}$Au$_{22.5}$Fe$_{0.5}$ specimens are shown in figure 1. Nearly all the Au atoms of the crystallized specimen exist in La$_2$Au phase, because the X-ray profile revealed that it was composed of La$_2$Au phase and a small amount of a phase in which Au atoms are hardly soluble. The curves on the left side of figure 1 are the results of the best fitting with the assumption that each spectrum consists of two Lorentzians with equal height and width. It seems that the spectra of the amorphous should be fitted to at least two independent Lorentzians as shown on the right side of figure 1. Any way, the apparent values of the width and quadrupole splitting (QS) are about 30% larger in the amorphous phase than in the crystallized one. The value of isomer shift (IS) are nearly the same (7.7 mm/s and 7.6 mm/s), which is close to the value (8.1 mm/s) in the dilute alloy obtained by $^{197}$Pt source experiment /3/. Such large positive values of IS suggest that a large amount of s electrons are transfered from La atoms to Au atoms.

![Fig. 1: Mössbauer spectra of $^{197}$Au at 18 K for amorphous and crystallized La$_{78}$Au$_{22.5}$Fe$_{0.5}$ (13 mg Au/cm$^2$) and amorphous La$_{78}$Au$_{22}$ (36 mg Au/cm$^2$).](image-url)

These results indicate that the atomic configurations around Au atoms are similar between the amorphous phase and La$_2$Au in which Au atoms have no direct contacts, although the overlapping of slightly different configurations is expected in the former phase from the asymmetry and broadening of the Mössbauer peaks.

The recoilless fraction of $^{197}$Au in the amor-
phous phase is about 14% smaller than that in the crystallized one, and the Debye temperatures for the two phases were estimated to be 123 K and 130 K, respectively.

Figure 2 shows the Mössbauer spectra of $^{57}$Fe in the amorphous (and microcrystalline) La-Au-0.5 at%Fe alloys, for which the values of apparent peak width, $IS$ and $QS$ were equal within experimental errors, suggesting that the nearest neighbours of Fe atoms are independent of Au concentration.

This is consistent with the fact that the Au atoms have no direct contacts, which is suggested from the radial distribution function by Logan $^4$. (Fe atoms are expected to be substitutional for Au atoms in the La-Au amorphous phase, considering the close values of the radii of Fe and Au atoms).

The shape of the absorption lines in figure 2 noticeably deviates from Lorentzian. Further, the average $QS$ remarkably decreases with increase of Fe content; the specimens with 1 at%Fe have $QS$ which is about 55% of that for the specimen with 0.5 at%Fe. These are probably due to a complex interaction of Fe atoms, the distance of which would be larger than the nearest neighbour distance.

Figure 3 exhibits the Mössbauer spectra of $^{197}$Au for splat-quenched 2.8 to 8.1 at%Au specimens. The 22 at%Au specimen was identified to be a homogeneous amorphous phase by the X-ray profile and the behaviour at superconducting transition $\gamma_5$. The specimens from 2.8 to 8.1 at%Au have X-ray profiles in which the diffuse diffraction patterns were overlapped on the crystalline peaks and their amount increased with increase of Au content. Therefore, their Mössbauer spectra are probably a superposition of those corresponding to Au atoms in supersaturated $\beta$ phase and those in the microcrystalline or amorphous phase.

Because the lattice parameter in the $\beta$ phase increases and the superconducting temperature decreases rapidly with increase of Au content $\gamma_5$, the specimens contain the solute Au atoms in the $\beta$ phase at least a part of which occupy the interstitial-type lattice sites.

The main difference between the spectra of 2.8 to 8.1 at%Au specimens and that of the 22 at%Au amorphous specimen exists in the vicinity of 10 mm/s, where the additional absorption of formers is not clearly observed in the latter spectrum. Such absorption is also not observed in the La$_2$Au phase as shown in figure 1. It is not clear that the absorption is a single peak or one of a doublet the other peak of which exists in lower velocity range. However, it probably has a larger value of $IS$ in either case than those of La$_2$Au and amorphous. Therefore, the absorption seems to correspond to interstitial Au atoms which have no direct contacts with each other. The interstitial clusters of Au atoms which have direct contacts as is in the case of dumb-bell
type interstitials may not have so large value of IS, because each Au atom in the clusters has less La neighbours and necessarily less transferred s electrons from La atoms. In order to explain the result that the fractional increment of the lattice parameter of β phase with Au content is one order of magnitude smaller than that of metal-metalloid solid solution /5/, the existence of substitutional Au atoms is necessary in addition to the isolated interstitials. Thus, it appears that the most preferable configuration of the solute in the supersaturated β phase of La-Au alloys is the coexistence of substitutional Au atoms and interstitial Au atoms which have no direct contacts. This situation is consistent with the fact that the La-Au alloy system has intermetallic compounds with high melting temperatures, which indicates that a La-Au bond is more favourable than a Au-Au bond.

Acknowledgements.— The authors are grateful to Pr. S. Nishikawa for his advice and encouragement. They also acknowledge the experimental assistance of Mr. K. Kawano. A part of this work was done under the Visiting Researchers Program of Kyoto University Research reactor Institute.

References

/5/ Nanao, S., Ohji, Y., Sugiura, J. and Ino, H., 3rd Int. Conf. on Rapidly Quenched Metals at Univ. of Sussex (1978).