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Physica B 208&209 (1995) 398–400

PHYSICA B

Comparative radial distribution analysis of the short range order in metallic glass $Al_{0.91}La_{0.09}$ and crystalline $Al_{11}La_3$

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Abstract

XAFS data of metallic glass $Al_{0.91}La_{0.09}$ and a crystalline phase $Al_{11}La_3$ formed by annealing of the glass were measured at the La L_3 edge at $T = 12$ K and analyzed using the radial distribution function method. The shortest La–Al distance appeared to be distinctively smaller within the glass than in the crystal. This difference decreases the disparity in size of La and Al in the alloy, allowing their mixing in the glassy state.

The metallic glass $Al_{0.91}La_{0.09}$ was recently synthesized by a melt-spinning method [1]. The purpose of the present work was to examine the structure of this alloy by XAFS for better understanding of the reason for the unusual glass formation at high concentrations of Al ($> 90\%$). We found that a small fraction of La–Al bonds in the glass shortened by 0.12 ± 0.05 Å as a result of the quenching process. This decreaes the size disparity of La and Al atoms, allowing their mixing into the single glassy phase.

We used both an X-ray diffraction method to characterize the samples and the RDF method of XAFS [2] (known also as the splice method) to study the local atomic environment around the central La atoms. This method has already been applied to several different materials including quasi-crystals [2]. We tested the RDF method first against the known structure ($Al_{11}La_3$) to check the reliability of the method in this application.

Amorphous ribbons of metallic glass $Al_{0.91}La_{0.09}$ were produced by melt spinning in the Technion (Israel) and rolled to 20 μm thickness to avoid the thickness effect in XAFS by satisfying the condition $\Delta\mu x \leqslant 1$, x being the sample thickness and $\Delta\mu$ the absorption L_3 edge step. The crystalline phase $Al_{11}La_3$ was obtained by annealing some of the ribbons. X-ray diffraction measurements showed large crystallites of Al and $Al_{11}La_3$ phases in the crystallized ribbons. The XAFS measurements on the La L_3 edge (photon energy is 5483 eV) were performed on the beamline XIIA at NSLS using a double crystal (1 1 1) Si monochromator. The data were obtained at 12 K. The AUTOBK code [3] was used to extract the atomic background for both glass and crystal data. The resultant $\chi(k)$, where k is the photoelectron wave number, was normalized to the L_3 edge jump. Special care was taken to determine correctly the $k = 0$ point. Since the photoelectron transition occurs to the first unoccupied level, the lowest possible wave number is the Fermi momentum k_f. To achieve the true $k = 0$ limit we determined the Fermi energy level while using FEFF5 theory [4] to subtract background [3] and then lowered the energy reference by E_f. The values of k_f and E_f are provided by FEFF5 for a given central atom. For the central atom La the values calculated by FEFF5 are: $k_f = 1.6$ Å^{-1}, $E_f = 9.7$ eV.

We calculated the radial distribution function $\rho(r)$ of the nearest Al neighbors to the central La atom by the

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SSDI 0921-4526(94)00700-4

RDF method [2] as follows:

$$\rho(r) = \frac{4r^2}{\pi r_s^2} \int_0^\infty |\chi'| \sin(2kr_s + \Delta\Psi) \sin(2kr)\, dk. \quad (1)$$

$|\chi'(k)|$ and $\Delta\Psi(k)$ are the amplitudes ratio and phase difference of the unknown and standard data sets, respectively. r_s is the mean interatomic distance in the standard data structure. To calculate the integral in Eq. (1) we used the cumulant expansion to extrapolate the signal to $k = 0$. To reduce the cutoff wiggles from the upper limit of the data range, k_2, we employed the Gaussian convergence factor $\exp(-2k^2\sigma_c^2)$. As a standard we used a theoretical XAFS signal generated by an individual photoelectron single scattering path La → Al with a half path length r_s, calculated with FEFF5. We determined r_s from the fit of the sum of FEFF5 paths between the central La and its different Al neighbors to the crystalline La_3Al_{11} XAFS data, where the distribution of atoms is known [5]. The fit of the theoretical χ to the crystal data was performed in r space (Fig. 1), using the program FEFFIT (University of Washington). To isolate the first shell the r range from 2.0 to 4.0 Å was chosen. The unknown crystal data $\chi_u(r)$ and the standard $\chi_s(r)$ were then back Fourier transformed to k space and their ratio $\chi'_u(k)$ was obtained. Since the crystal structure is known, a theoretical $\chi'_{th}(k)$ was calculated in a straighforward manner, assuming that all nine paths to Al atoms within the first shell have the same scattering amplitude and phase shifts. The coordination number, defined as the area below the RDF curve, is equal to the correct value of 16 for the model calculation $\chi'_{th}(k)$ and 16.0 ± 0.2 for the experimental crystal data $\chi'_u(k)$. The centroid of $\rho(r)$ is at 3.32 ± 0.30 Å.

Changing the convergence factor gradually from 0.015 Å^2 to zero we resolved more and more structure for the crystal data. We found that the convergence factor affected the shape and the width of the distribution $\rho_{th}(r)$ dramatically. To demonstrate the splitting into subshells in the theoretical RDF and to avoid the cutoff wiggles we expanded an analytical $\chi'_{th}(k)$ far away in k space (up to 50 Å^{-1}) where no covergence factor was needed. The required vanishing of $\chi'_{th}(k)$ is provided by thermal DWF only. The spatial resolution is 0.01 Å.

The agreement between theory and data is good, varifying the accuracy of applying this method to the glass $Al_{0.91}La_{0.09}$. The RDF was obtained the same way as for the crystal. Calculations of the coordination number and the average La–Al distance over the shell gave the following results:

$$N = 14.45 \pm 0.10, \quad \langle R_{La-Al} \rangle = 3.33 \pm 0.05 \text{ Å}.$$

To study how the convergence factor affects the RDF of the glass we varied it from 0.015 Å^2 to 0 and compared the resultant RDFs. It turned out that the RDFs look similar and almost no change in the broadening may be noticed, in contrast to the crystal. Now, comparing the two RDFs for the glass and the crystal we conclude that the distribution of atoms in the glass shows some shorter bonds than the crystal allows below 3.16 Å. Evaluating the number of atoms contained in the glass within the distances below 3.16 Å (the distance to the left wing of the RDF for crystal, Fig. 2) we find $N = 1.7 \pm 0.1$, giving the mean number of the short bonds in the glass. The mean short bond length is found to be 3.09 ± 0.05 Å.

In conclusion we find a large change in $\rho(r)$ between the glass and the phase that crystallizes from it. The glass $\rho(r)$ shows some bonds shorter than found in the crystalline phase. It is suggested that this shortening is

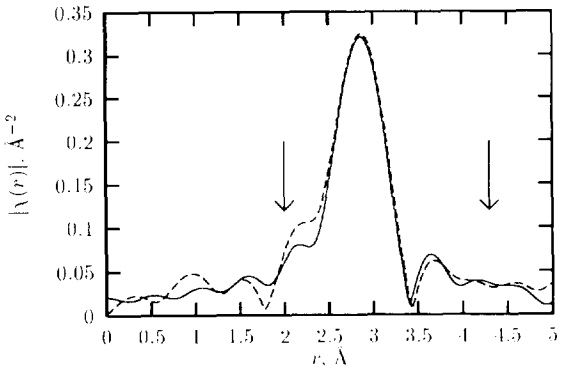

Fig. 1. Fit of the FEFF theory (solid) to the crystal $Al_{11}La_3$ data (dashed). Initial data k range from 2.5 to 10.5 Å^{-1} (while transformed k range from 0 to 10.5 Å^{-1}). Fitting r range is shown by arrows.

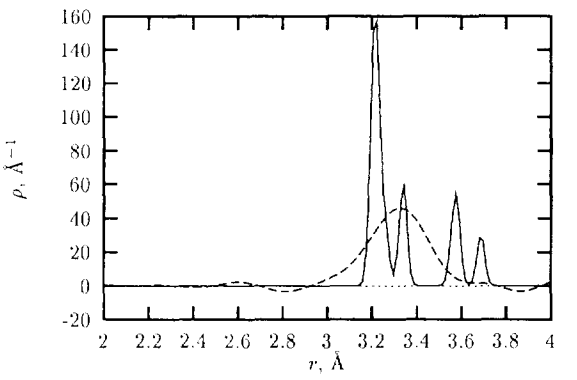

Fig. 2. RDF for the glass $Al_{0.91}La_{0.09}$ (dash) and the theory for crystal La_3Al_{11} (solid).

important in understanding the unusual properties of the $Al_{0.91}La_{0.09}$ glass, including its formation at such low La concentrations.

The calculation of the radial distribution functions was performed using the program RDF. This work was supported in part by the US–Israel BSF Grant No. 90-00152/1 and by the DOE Grant No. DE-FG06-90ER45425.

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