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^{57}Fe Mössbauer Study of Amorphous and Icosahedral $Zr_{65}Al_{7.5}Ni_{10}Cu_{7.3}Fe_{0.2}Ag_{10}$

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The alloys $Zr_{65}Al_{7.5}Ni_{10}Cu_{7.3}Fe_{0.2}Ag_{10}$ in the amorphous and icosahedral state have been studied with ^{57}Fe Mössbauer spectroscopy in the temperature range 77–300 K. The average quadrupole splitting decreases with temperature as $T^{3/2}$ and is significantly larger for the icosahedral alloy. The quadrupole splitting in the icosahedral alloy is the largest ever reported for a metallic system. The vibrations of the Fe atoms in both alloys are well described by a simple Debye model.

Introduction

Amorphous (*a*) alloys (glasses) are generally produced from an undercooled liquid state by rapid quenching techniques or quasi-statically at slow cooling. The latter technique has recently led to the development of multicomponent metallic glasses with large glass forming ability and a wide supercooled liquid region before crystallization[1]. Very recently, an icosahedral (*i*) phase has been discovered in a Zr-Al-Ni-Cu-Ag metallic glass annealed in a wide supercooled temperature range[2-4]. Although there are no structural models for the *a*-Zr-Al-Ni-Cu-Ag alloys, it has been speculated[2] that the structure of these alloys is an assembly of randomly oriented *i* clusters which presumably are also the structural units in *i*-Zr-Al-Ni-Cu-Ag alloys.

This paper reports on a ^{57}Fe Mössbauer spectroscopy (MS) study of the *a* and *i* alloys $Zr_{65}Al_{7.5}Ni_{10}Cu_{7.3}Fe_{0.2}Ag_{10}$. It is demonstrated that the hyperfine-interaction parameters are significantly different for these two alloys. It is argued that the structure of the *a* alloy cannot be described in terms of a micro-quasicrystalline model. It is shown that the vibrations of the Fe atoms in both alloys are, surprisingly, well described by a simple Debye model.

Experimental Procedure

An alloy of nominal composition $Zr_{65}Al_{7.5}Ni_{10}Cu_{7.3}Fe_{0.2}Ag_{10}$ was prepared by arc melting in an argon atmosphere of high-purity elemental constituents; the Fe metal used was enriched to 95.9% in the ^{57}Fe isotope. Amorphous ribbons were prepared by melt spinning. The amorphous nature of the ribbons was confirmed with x-ray diffraction and electron microscopy experiments. The differential scanning calorimetry measurements at a heating rate of 0.67 K/s revealed a glass transition temperature at 652 K and two crystallization temperatures at 706 and 769 K associated with two exothermic peaks[2,3]. The *a* ribbons were annealed at 570 K for 15 min. This resulted in the appearance of nanoscale spherical *i* precipitates, as conformed with the electron microscopy and x-ray diffraction measurements[2-4].

^{57}Fe MS measurements were carried out in the temperature range 77–300 K using a standard Mössbauer spectrometer operating in a sine mode[5]. The spectrometer was calibrated with a 6.35-μm Fe foil, and the spectra were folded. The Mössbauer absorbers of the *i* and *a* alloys had the same surface density of 0.043 mg $^{57}Fe/cm^2$. This corresponds to an effective thickness parameter[5] at 299 K of 0.852 and 0.920 (using the values of the absorber Debye-Waller factors, f_a and f_i, of 0.732 and 0.791 determined below), respectively. As the resulting Mössbauer spectra are due to a multiple of elementary quadrupole doublets, the effective thickness parameter spreads over them and therefore the absorbers can be regarded as being thin[5].

Results and Discussion

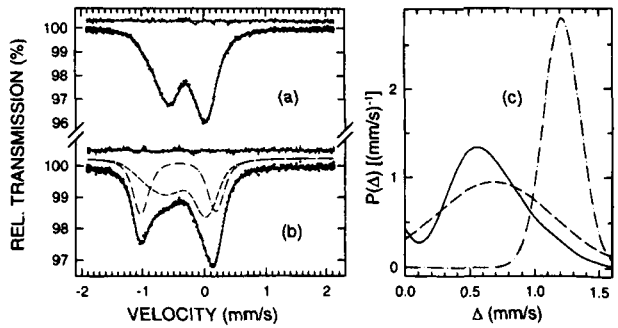

Fig. 1. ^{57}Fe Mössbauer spectra at 299 K of (a) *a* and (b) *i* alloys $Zr_{65}Al_{7.5}Ni_{10}Cu_{7.3}Fe_{0.2}Ag_{10}$ fitted [solid lines in (a) and (b)], respectively, with one P(Δ) component [solid line in (c)] and two P(Δ) components [dashed and dot-dashed lines in (c)]. The component fitted spectra are also shown in (b). The residuals are shown above each spectrum.

The Mössbauer spectrum of the *a* alloy consists of a broadened asymmetric doublet [Fig. 1(a)] which results from the distribution of the quadrupole splittings, P(Δ). It was fitted with the constrained version[6] of the Hesse-Rübartsch method. An asymmetry of the spectrum was accounted for by assuming a linear relation between the centre shift, δ, and Δ of the elementary Lorentzian doublets with width of 0.230 mm/s. A good fit, as judged by the value of χ^2=1.15 and by the residuals [Fig. 1(a)] was obtained for the distribution P(Δ) shown in Fig. 1(c). It would be desirable to compare this distribution with the one calculated for a structural model of the Zr-Al-Ni-Cu-Ag glasses. Unfortunately, such a model has not been proposed yet for these new *a* alloys.

The Mössbauer spectrum of the *i* alloy [Fig. 1(b)] can only be fitted with two subspectra[7]. The hyperfine parameters and the distribution P(Δ) of the first subspectrum [Fig. 1(c)] are very close to those corresponding to the *a* alloy. This is consistent with the fact that the *i* sample consists of nanoscale *i* clusters embedded in the *a* matrix. The weight fraction of the *i* phase calculated from the relative area of the subspectrum and the values of f_a and f_i is 41(4)%, which is in agreement with the value obtained from the transmission electron microscopy image of this sample[7]. The second subspectrum results from the *i* phase present in the *i* sample. Its remarkable feature is the very large value of the average quadrupole splitting, $\overline{\Delta}$, which is the largest ever observed for any quasicrystalline alloy[8] and, to the best of our knowledge, the largest ever found for any metallic alloy. Such a high value of $\overline{\Delta}$ indicates an unusually asymmetric atomic environment around the Cu atoms in the *i* phase. The fact that the distribution P(Δ) corresponding to the *i* phase is completely different from that corresponding to the *a* phase [Fig. 1(c)] indicates that the structure of a-Zr-Al-Ni-Cu-Ag alloys cannot be described in terms of a micro-quasicrystalline model.

The distributions P(Δ) similar to those in Fig. 1 (c) were determined from the fits of the *a* and *i* samples measured at other temperatures. The temperature dependence of $\overline{\Delta}$ could be fitted [Fig. 2(a)] to the equation $\overline{\Delta}(T)=\overline{\Delta}(0)-BT^{3/2}$, where $\overline{\Delta}(0)$ is the value of $\overline{\Delta}$ at 0 K and B is a constant. Such a temperature dependence has been observed in many noncubic metallic alloys. The values of $\overline{\Delta}(0)$, B determined from the fits for the *a* and *i* phases are respectively 0.6847(20) mm/s, $1.489(88)\times10^{-5}$ $K^{-3/2}\cdot$mm/s and 1.2610(29) mm/s, $1.122(69)\times10^{-5}$ $K^{-3/2}\cdot$mm/s.

The average centre shift at temperature T, $\overline{\delta}(T)$, determined from the fits of the spectra of the *a* and *i* samples is given by $\overline{\delta}(T)=\delta_o+\delta_{SOD}(T)$, where δ_o is the intrinsic isomer shift and $\delta_{SOD}(T)$ is the second-order Doppler shift which depends on lattice vibrations of the Fe atoms[5]. In terms of the Debye approximation of the lattice vibrations, $\delta_{SOD}(T)$ is expressed[9] by the characteristic Mössbauer temperature Θ_M. By fitting the experimental data

$\overline{\delta}(T)$ [Fig. 2(b)] to the expression $\overline{\delta}(T) = \delta_o + \delta_{SOD}(T)$, the quantities δ_o and Θ_M can be determined. They are −0.1464(35) mm/s, 379(29) K and −0.3034(29) mm/s, 439(28) K, respectively, for the *a* and *i* samples. The corresponding values of f_a and f_i at 299 K are 0.732(36) and 0.791(24). The different values of δ_o indicate that electronic properties of the *a* and *i* alloys are very different.

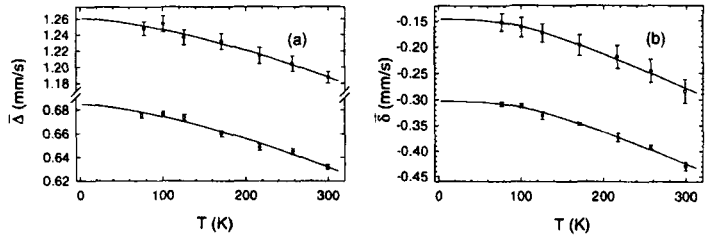

Fig. 2. (a) Temperature dependence of the average quadrupole splitting of the *a* (open circles) and *i* (closed circles) alloys $Zr_{65}Al_{7.5}Ni_{10}Cu_{7.3}Fe_{0.2}Ag_{10}$. The solid lines are the fits, as explained in the text. (b) Temperature dependence of the average centre shift (relative to α-Fe) of the *a* (open circles) and *i* (closed circles) alloys. The solid lines are the fits, as explained in the text.

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