

Magnetic behaviour and hyperfine interactions in Al–Fe–Ce metallic glasses

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⁵⁷Fe Mossbauer effect and magnetic susceptibility measurements have been performed on the new glassy alloys Al₉₀Fe₅Ce₅, Al₈₇Fe_{6.7}Ce_{6.3}, Al₈₇Fe_{8.7}Ce_{4.3}, and Al₈₇Fe_{9.3}Ce_{3.7}. It is found that Fe atoms are not magnetically ordered in the Fe-rich glasses down to 4.2 K. The disorder inherent to glasses is manifested in the distribution of the electric quadrupole splittings, which is shown to be well described by a Gaussian shape. The magnetic susceptibility of the alloys follows the Curie–Weiss law between 4.2 K and room temperature. The small effective magnetic moment values suggest mixed-valence behaviour.

1. Introduction

Metallic glasses have been widely studied for the past few decades. In particular, Al-based glasses have been studied since they are of special technological interest because of their lower density as compared with that of other alloys. In most binary glassy systems, A_{100-x}B_x, glasses form for only 5 < x < 85. Recently, a new series of rare-earth-containing metallic Al-rich glasses has been discovered [1,2]. These glasses contain up to 90 at.% Al and they exhibit excellent mechanical properties. For example, their tensile strength exceeds that of the strongest commercial Al alloys [1,2].

While the mechanical, structural, and stability characteristics of these novel alloys, and in particular of the Al–Fe–Ce glasses of interest here, have been studied extensively [1–3], there are only a few reports of investigations of their physical properties. From magnetic susceptibility measurements, Wagner et al. [4] found that for

Al₈₇Fe_{8.7}Ce_{4.3} the effective magnetic moment, μ_{eff} , is 1.37 μ_{B} (per Ce, i.e. assuming that Fe does not have a localized moment) at room temperature and about 0.25 μ_{B} at 5 K. This has been interpreted [4] as evidence of a significant mixed-valence behaviour in this glassy alloy. On the other hand, Dunlap et al. [5] found that Al₉₀Fe₅Ce₅ has a very small magnetic susceptibility, χ , resulting in $\mu_{\text{eff}} = 0.02\mu_{\text{B}}$ (per Fe). It is surprising that such small changes in the composition of Al–Fe–Ce glassy alloys can lead to such dramatic changes in their magnetic properties. These authors [5] also measured a room-temperature Mössbauer spectrum of Al₉₀Fe₅Ce₅ and concluded that the distribution of the quadrupole splittings, $P(\Delta)$, can be suitably described by the shell model.

The purpose of this paper is to report on the hyperfine interactions and the susceptibility data for several Al–Fe–Ce glassy alloys, including the two studied in refs. [4,5].

2. Experimental procedure

Ingots of composition Al₉₀Fe₅Ce₅, Al₈₇Fe_{6.7}Ce_{6.3}, Al₈₇Fe_{8.7}Ce_{4.3}, and Al₈₇Fe_{9.3}Ce_{3.7} were

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prepared by arc-melting in an argon atmosphere of high-purity elemental constituents. The ingots were melt-spun by ejecting molten alloy through a 0.8 mm orifice in a quartz tube and using a 70 kPa overpressure of argon. The molten alloy impinging upon a circumferential surface of a copper wheel rotating with a tangential velocity of 40 m/s in a helium atmosphere. The resulting ribbons were about 3 mm wide and up to 2 m long.

Room-temperature X-ray diffraction (XRD) measurements of the as-quenched samples were conducted on a Siemens D500 scanning diffractometer using Cu K α radiation. ^{57}Fe Mössbauer effect (ME) measurements were performed at room temperature and/or at 4.2 K using a Wissel MSII Mössbauer spectrometer operating in the sine or triangular mode. The spectrometer was calibrated with a 12.9 μm Fe foil, and the spectra were folded. The full linewidth at half maximum, Γ , of the inner pair of the α -Fe Zeeman pattern was 0.241(1) mm/s. The surface densities of the Mössbauer absorbers corresponding to $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$, $\text{Al}_{87}\text{Fe}_{87}\text{Ce}_{43}$ and $\text{Al}_{87}\text{Fe}_{93}\text{Ce}_{37}$ were, respectively, 1.13, 1.62 and 2.56 mg Fe/cm 2 ; the source was $^{57}\text{Co}(\text{Rh})$. Magnetic susceptibility measurements were conducted using a vibrating-sample magnetometer operating with a Mössbauer-type drive in a continuous flow cryostat in the temperature range 4.2–295 K and in a magnetic field of 1.75 T. The magnetization signal was recorded during warm-up at a rate of about 1 K/min below 15 K and up to 5 K/min at higher temperatures. The sensitivity of the set-up deteriorates below 10 K and therefore it was not feasible to detect any possible spin-glass behaviour at low temperatures. Magnetization measurements at room temperature in the fields up to 1.75 T were performed to detect magnetic ordering of the samples caused by the possible presence of magnetic impurities.

3. Results and discussion

The XRD patterns were very similar to those observed earlier [2], thus confirming the amorphous nature of the alloys. For the alloys $\text{Al}_{87}\text{Fe}_{87}\text{Ce}_{43}$ and $\text{Al}_{87}\text{Fe}_{93}\text{Ce}_{37}$ the peak at

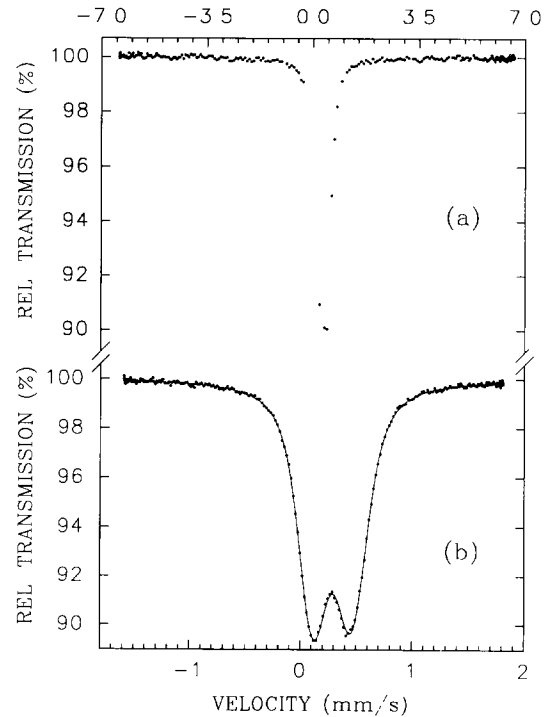


Fig 1 ^{57}Fe Mössbauer spectra of $\text{Al}_{87}\text{Fe}_{93}\text{Ce}_{37}$ at 4.2 K measured for a large velocity range (a) and a small velocity range (b) The solid line in (b) is the fit, as described in the text The velocity scale is relative to α -Fe

$2\theta \approx 38^\circ$ also exhibited a shoulder, as reported earlier [2].

For the glassy alloy with the highest Fe concentration, $\text{Al}_{87}\text{Fe}_{93}\text{Ce}_{37}$, the ^{57}Fe ME spectrum was measured at 4.2 K over a large velocity range (fig. 1(a)) in order to detect a Zeeman pattern which is expected if the Fe atoms are magnetically ordered or, what is more probable, frozen in a spin-glass state. The absence of such a pattern in fig. 1(a) proves that the Fe atoms are not magnetically ordered down to this temperature. The 4.2 K spectrum of this alloy, but measured for a smaller velocity range (fig. 1(b)), exhibits two broad lines resulting from the distribution, $P(\Delta)$, of the quadrupole splittings, Δ , and characteristic for the ME spectra of materials without long-range crystalline order (amorphous and quasicrystalline alloys) [6]. In order to determine the shape of this distribution, the spectrum in fig. 1(b) was fitted using a recently proposed method for deriving $P(\Delta)$ of arbitrary shape [7]. This

method is based on representing the true distribution as a sum of Gaussian components and the corresponding spectra are sums of Voight lines. The asymmetry of the Mössbauer spectrum was taken into account by assuming a linear dependence $\delta = \delta_0 + a\Delta$ between the isomer shift (relative to α -Fe) δ , and Δ , where δ_0 and a are fitted parameters. A good fit could be obtained with only one Gaussian component (fig. 1(b)). The values of the fitted parameters $\bar{\Delta}$ (the center of the Gaussian distribution of Δ , i.e. the mean of Δ), σ_{Δ} (the Gaussian width; the full width at half maximum of $P(\Delta)$ is $2(2 \ln 2)^{1/2}\sigma_{\Delta}$), δ_0 , a , $\bar{\delta}$ (the mean of δ), Γ (the full width at half maximum of the elemental Lorentzian lines), and of χ^2 defined in the usual way [6], are given in table 1. The distributions $P(\Delta)$ and $P(\delta)$ corresponding to the fit are shown in fig. 2. The Gaussian width of the distribution of the isomer shift $P(\delta)$ is $\text{abs}(a\sigma_{\Delta})$.

^{57}Fe Mössbauer spectra of other Al-Fe-Ce samples are also well fitted with a single Gaussian component. As an example, the fits of the room-temperature and 4.2 K spectra of $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ are shown in fig. 3, and the corresponding distributions are given in fig. 4. The values of the corresponding fitted parameters for $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ and $\text{Al}_{87}\text{Fe}_{8.7}\text{Ce}_{4.3}$ are presented in table 1.

The data in table 1 lead to several observations. First, whereas there are relative changes of $\bar{\Delta}$ of up about 10%, there are essentially no changes of $\bar{\delta}$ with composition. Both the $\bar{\Delta}$ and σ_{Δ} values are similar to those found in other disordered alloys [5,6,8]. Second, the decrease of $\bar{\Delta}$ with increasing temperature is in line with the decrease observed both in disordered [6,8] and crystalline [9] materials. The temperature de-

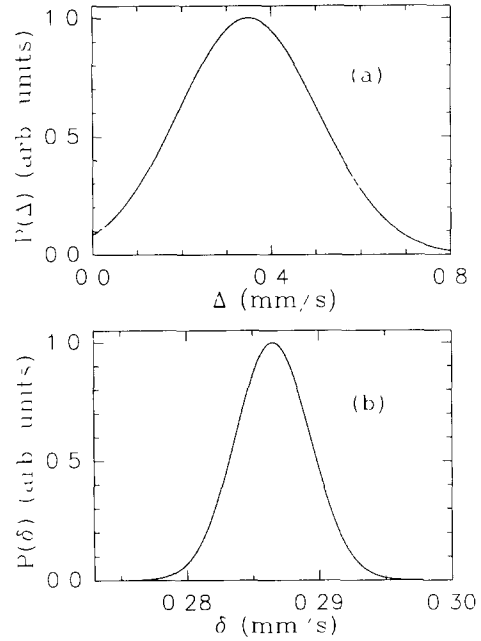


Fig 2 The distribution functions $P(\Delta)$ (a) and $P(\delta)$ (b) corresponding to the fit in fig 1(b)

crease of $\bar{\delta}$ results from the second-order Doppler effect [10]. Third, the fits of the Mössbauer spectra of the Al-Fe-Ce glasses using other shapes of the $P(\Delta)$ distribution [11] lead to the conclusion that a Gaussian shape is the best description of the experimental spectra. It would be desirable to compare the distributions $P(\Delta)$ derived from the Mössbauer spectra with the calculated distributions for a given local structural model for Al-Fe-Ce metallic glasses. A calculation of $P(\Delta)$, especially in systems without long-range periodicity, is a complex and challenging endeavour. First-principles calculations of $P(\Delta)$ are rare, and those available were performed for simple crystalline systems.

Table 1

Parameters derived from the one-Gaussian-component fit of the Mossbauer spectra of the Al-Fe-Ce glassy alloys. The meaning of the symbols is explained in the text

Sample	T (K)	$\bar{\Delta}$ (mm/s)	σ_{Δ} (mm/s)	δ_0 (mm/s)	a	$\bar{\delta}$ (mm/s)	Γ (mm/s)	χ^2
$\text{Al}_{90}\text{Fe}_5\text{Ce}_5$	295	0.312(1)	0.135(1)	0.154(3)	0.046(1)	0.169(1)	0.236(1)	1.43
	4.2	0.332(1)	0.143(4)	0.275(2)	0.020(4)	0.282(2)	0.239(5)	0.94
$\text{Fe}_{87}\text{Fe}_{8.7}\text{Ce}_{4.3}$	4.2	0.366(1)	0.205(2)	0.285(1)	0.003(2)	0.286(2)	0.266(1)	0.93
$\text{Al}_{87}\text{Fe}_{9.3}\text{Ce}_{3.7}$	4.2	0.348(1)	0.157(1)	0.280(1)	0.018(2)	0.287(1)	0.230(1)	1.12

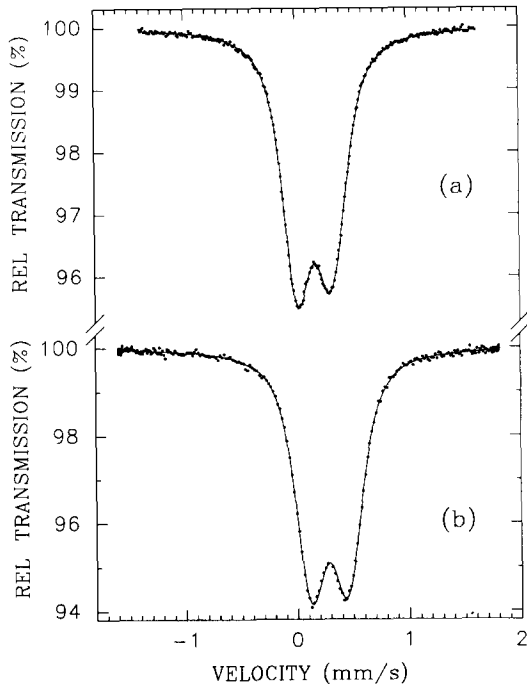


Fig. 3. ^{57}Fe Mössbauer spectra of $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ at 295 K (a) and 42 K (b). The solid lines are the fits, as described in the text. The velocity scale is relative to $\alpha\text{-Fe}$.

The temperature dependence of the magnetic susceptibility (fig. 5) follows the Curie-Weiss law. To allow for the possible presence in the samples of a small amount of a ferromagnetic impurity with the magnetization M_0 , the equation $\chi = \chi_P + C/(T - \Theta) + M_0(1 - aT^{3/2})/H$ was used [12], where the symbols have their usual meaning. Note that the temperature-independent susceptibility obtained from the fit of the $\chi(T)$ dependence cannot be associated with the Pauli susceptibility if M_0/H cannot be neglected. The data shown in fig. 5 were fitted to the equation [12]

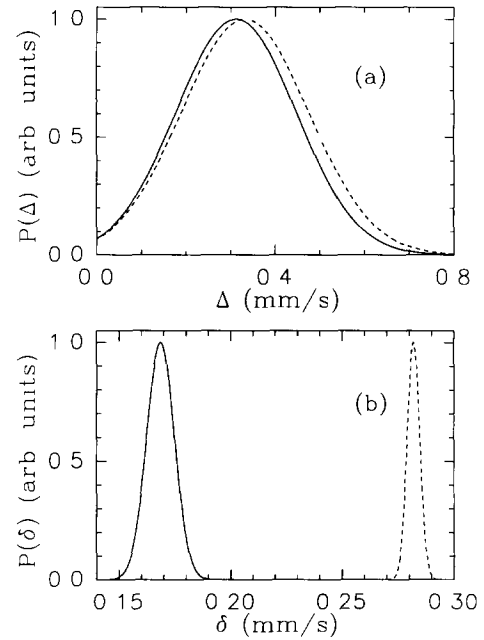


Fig. 4. The distribution functions $P(\Delta)$ (a) and $P(\delta)$ (b) corresponding to the fits in fig. 3(a) (solid lines) and fig. 3(b) (dashed lines).

$\chi = a_0 + C(T - \Theta) + a_3T^{3/2}$, where $a_0 = \chi_P + M_0/H$ and $a_3 = -aM_0/H$. The results of the fit are listed in table 2.

The magnetization measurements could not detect the presence of any magnetic ordering due to the possible magnetic impurities. This is consistent with the negligibly small value of a_3 (table 2). Thus the temperature-independent susceptibility obtained from the fit can be interpreted as the Pauli susceptibility. Metallic systems with Ce exhibit many unusual characteristics, such as valence fluctuations or superconductivity, due to the special nature of the 4f electrons of Ce [13].

Table 2

Parameters obtained from the fit of the temperature dependence of the magnetic susceptibility of the Al-Fe-Ce glassy alloys. The meaning of the symbols is explained in the text

Sample	χ_P (10^{-6} cm ³ /g)	C (10^{-6} (cm ³ /g) K)	Θ (K)	a_3 (10^{-10} cm ³ / (g K ^{3/2}))	$\mu_{\text{eff}}^{\text{Ce}}$ (μ_B)	$\mu_{\text{eff}}^{\text{Fe}}$ (μ_B)	$\mu_{\text{eff}}^{\text{Ce,Fe}}$ (μ_B)
$\text{Al}_{90}\text{Fe}_5\text{Ce}_5$	3.40(34)	8.20(57)	-4.5(6)	-0.64(9)	0.19(1)	0.19(1)	0.13(1)
$\text{Al}_{87}\text{Fe}_{6.7}\text{Ce}_{6.3}$	4.11(41)	46.75(71)	-7.4(2)	-2.57(3)	0.46(1)	0.45(1)	0.32(1)
$\text{Al}_{87}\text{Fe}_{8.7}\text{Ce}_{4.3}$	2.82(28)	32.63(58)	-9.8(2)	-1.32(2)	0.46(1)	0.32(1)	0.26(1)
$\text{Al}_{87}\text{Fe}_{9.3}\text{Ce}_{3.7}$	2.48(25)	9.00(27)	-2.9(2)	-1.01(4)	0.26(1)	0.16(1)	0.14(1)

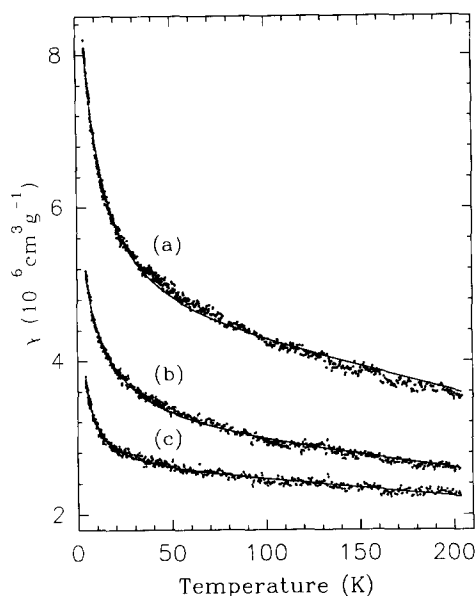


Fig. 5. Temperature dependence of the magnetic susceptibility of $\text{Al}_{87}\text{Fe}_{67}\text{Ce}_{63}$ (a), $\text{Al}_{87}\text{Fe}_{87}\text{Ce}_{43}$ (b) and $\text{Al}_{87}\text{Fe}_{93}\text{Ce}_{37}$ (c). The solid lines are the fits, as described in the text.

The valency of Ce in most metallic environments is always close to three [13], which corresponds to $\mu_{\text{eff}} = 2.54\mu_{\text{B}}$ per Ce atom. Since no magnetic impurities are present in the samples studied, it is reasonable to assume that the finite value of the Curie constant (table 2) implies the existence of a localized moment on Ce atoms, $\mu_{\text{eff}}^{\text{Ce}}$ (table 1), assuming no localized moment on Fe. If, on the other hand, one assumes [5] that the moment is localized on the Fe atoms, which seems to be much less probable (since Fe diluted in Al bears no magnetic moment and because the dependence of C on Fe concentration observed here does not follow the composition dependence expected for a paramagnet with a magnetic moment localized on Fe), then this leads to the values of $\mu_{\text{eff}}^{\text{Fe}}$ given in table 2. One cannot also exclude the possibility that the moment is localized on both the Ce and Fe atoms ($\mu_{\text{eff}}^{\text{Ce,Fe}}$ values in table 2). In any case, our susceptibility results could be interpreted as indication of the mixed-valence behaviour in the Al-Fe-Ce glassy alloys, which was first suggested by Wagner et al. [4]. However, in view of the widely different values of C, Θ , and χ_{P} obtained for nominally the same compositions

($\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ and $\text{Al}_{87}\text{Fe}_{87}\text{Ce}_{43}$) here and in other studies [4,5], further investigations of these interesting glassy alloys are necessary.

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