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SUBSTITUTIONAL SITE PREFERENCE IN Al—Cu—Ge—Mn ICOSAHEDRAL ALLOYS

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Evidence is presented, based on analyses of ^{57}Fe Mössbauer spectra of magnetically ordered Al-Cu(Fe)-Ge-Mn icosahedral alloys measured at 4.2 K, for the dependence of Fe substitution upon the concentration of Fe. It is found that Fe substitutes approximately randomly on transition-metal (TM) sites, i.e., it enters both magnetic and nonmagnetic class of sites, for very small concentration of Fe. However, for larger concentration, Fe enters preferentially the nonmagnetic class of sites. This is discussed in terms of recent theoretical calculations which predict the dependence of a magnetic moment of a TM atom upon the volume associated with it in an alloy.

1. INTRODUCTION

The notion of two separate **classes** of Mn sites in paramagnetic Al-Mn-Si icosahedral alloys (IA), distinguished by the presence or absence of a localized magnetic moment, was established on the basis of the results obtained from ^{55}Mn NMR, ^{57}Fe Mössbauer, and magnetic susceptibility measurements /1-4/. As has been often emphasized in the literature /1,3,5/, the notion of two classes of TM sites should not be confused with the existence of two well-defined structural environments. Instead it implies the presence of two distributions of sites that span a whole range of local environments; this is supported by the observation with NMR or the Mössbauer effect of a continuous distribution of hyperfine interaction parameters. Previous analyses /6,7/ of ^{57}Fe Mössbauer spectra of IA in terms of two distinct TM crystallographic sites (the so called two-site model) were shown /5,8-10/ to be methodologically incorrect. In addition, the two-site model, which is based on the simplest interpretation of the three-dimensional Penrose tiling, is incompatible with the notion of a quasicrystal which by its very nature has an infinite number of distinct crystallographic sites /11/.

The first direct evidence for the presence of two classes of TM sites in magnetically ordered Al-Mn(Fe)-Ge and Al-Mn-Cu(Fe)-Ge IA has been presented in a recent ^{57}Fe Mössbauer study /12/ in which it was shown that 4.2 K Mössbauer spectra could be analyzed in terms of a nonmagnetic and magnetic component. Thus, the two classes of TM sites are present in both paramagnetic and magnetically ordered IA.

There is experimental evidence /13,14/ for **very small** amounts of Fe atoms substituting randomly for Mn atoms in Al-Mn-Si IA, i.e., they enter into both the magnetic and nonmagnetic class of sites, whereas for higher Fe concentration, they preferentially enter the nonmagnetic class of sites. The purpose of this paper is to investigate whether such a phenomenon also occurs in magnetically ordered IA.

2. EXPERIMENTAL

Ingots of icosahedral alloys $Al_{40}Mn_{25}Cu_{10-x}Fe_xGe_{25}$ (x = 0.06 and 3) were prepared by arc melting of high-purity elemental constituents under argon atmosphere. For the composition x = 0.06, the iron metal enriched to 95% in the ^{57}Fe isotope was used. The samples were produced according to the procedure described elsewhere /12/ and their x-ray diffraction

spectra were thoroughly analyzed /12,15/.

^{57}Fe Mössbauer measurements were carried out at room temperature and at 4.2 K using a Wissel MSII spectrometer operating in a sine mode. The spectrometer was calibrated with a 12.7-μm Fe foil and the spectra were folded. The surface densities of the x = 0.06 and 3 Mössbauer absorbers were respectively $4.0 \cdot 10^{-3}$ and $7.5 \cdot 10^{-3}$ mg ^{57}Fe/cm^2; the absorbers can therefore be regarded as thin ones.

3. RESULTS AND DISCUSSION

The analysis of the x-ray diffraction spectra and of the temperature dependence of magnetization /12,15/ shows that the $Al_{40}Mn_{25}Cu_{10-x}Fe_xGe_{25}$ samples contain a small amount of a ferromagnetic impurity which is responsible for the high value of the ordering temperature, T_c /16/. The value of T_c corresponding to the samples studied here is below 100 K /15/.

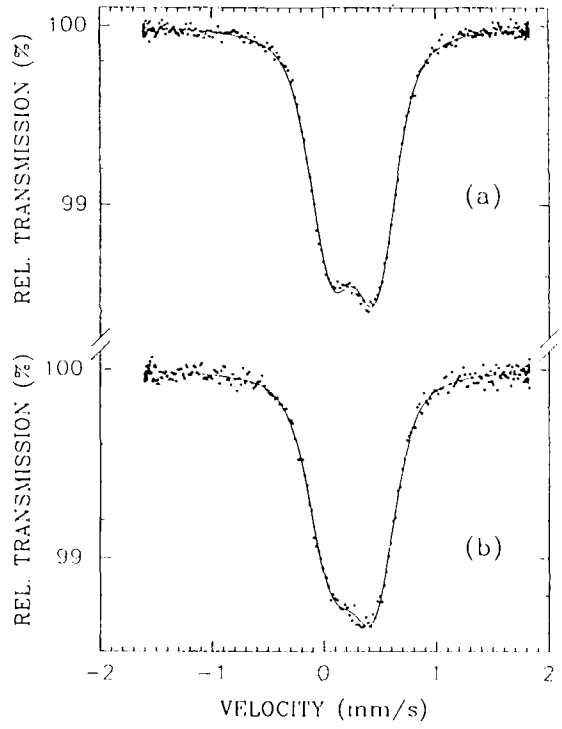

Fig. 1. Room-temperature ^{57}Fe Mössbauer spectra of $Al_{40}Mn_{25}Cu_{9.94}Fe_{0.06}Ge_{25}$ (a) and $Al_{40}Mn_{25}Cu_7Fe_3Ge_{25}$ (b). The solid line is a least-squares fit with a single Gaussian model as described in the text.

Room-temperature Mössbauer spectra of the studied samples (Fig. 1) clearly show a doublet structure, characteristic of paramagnetic IA, which is due to the electric quadrupole interaction, E2. The full linewidth at half maximum, Γ, of two Lorentzian lines obtained from a fit with an asymmetric doublet is about two times larger than Γ_{nat}. This is a clear evidence for the existence of the distribution $P(\Delta)$ of the quadrupole splittings Δ. The spectra were fitted using a recently proposed method /17/ for obtaining an arbitrary-shape $P(\Delta)$ equal to

a sum of Gaussian components. The asymmetry of the spectra (Fig. 1) was taken into account by assuming a linear coupling between the isomer shift (relative to α-Fe) δ and Δ, $\delta = \delta_0 + a\Delta$, where δ_0 and a are fitted parameters. Good fits were obtained with only one Gaussian component (Fig. 1) and the values of χ^2 were better than those obtained using a shell model /15/. The values of fitted parameters σ_Δ, $\bar{\Delta}$, δ_0, a, and $\bar{\delta}$ for the x = 0.06 sample are 0.265(3) mm/s, 0.398(2) mm/s, 0.274(1) mm/s, -0.025(3), and 0.264(2) mm/s. The corresponding parameters for the x = 3 sample are 0.285(6) mm/s, 0.381(3) mm/s, 0.273(2) mm/s, -0.038(4), and 0.259(2) mm/s. The standard deviation σ_δ corresponding to the Gaussian distribution of δ is equal to $a\sigma_\Delta$. The values of Γ for both fits are about 0.220 mm/s. The P(Δ) distribution is wider for the x = 3 sample than for the x = 0.06 one, which is in accordance with a larger degree of disorder expected for a higher substitution of Cu by Fe.

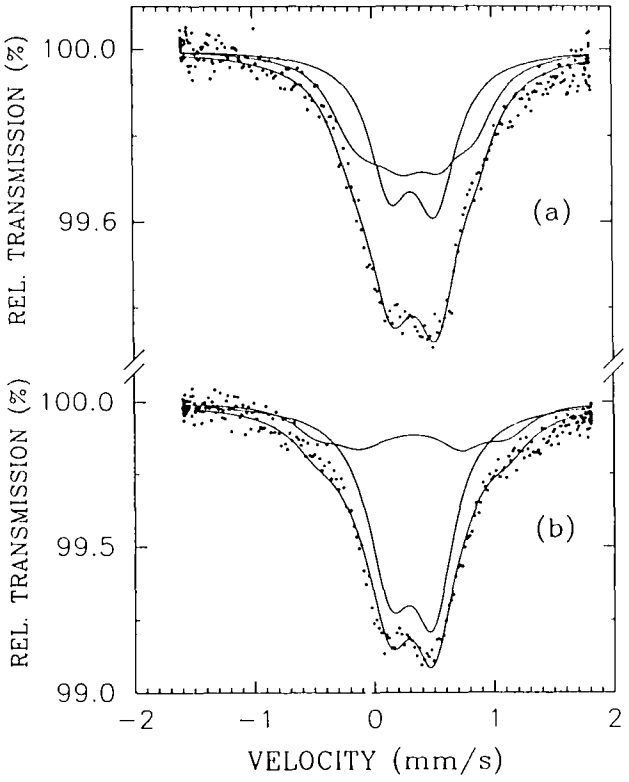

Fig. 2. 4.2 K ^{57}Fe Mössbauer spectra of $Al_{40}Mn_{25}Cu_{9.94}Fe_{0.06}Ge_{25}$ (a) and $Al_{40}Mn_{25}Cu_7Fe_3Ge_{25}$ (b). The solid line is a least-squares fit with two subspectra, which are also shown, as explained in the text.

The 4.2 K Mössbauer spectra (Fig. 2) show a significant broadening compared to room-temperature spectra (Fig. 1), which is caused by the simultaneous presence of comparable strength E2 and magnetic dipole interaction M1. Consequently, such spectra cannot be fitted using first-order perturbation theory. They were fitted using the algorithm given by Blaes et al. /18/, which is suitable for IA /12,15/. The 4.2 K Mössbauer spectra could not be fitted successfully with a one-component fit since they clearly exhibit some structure. A good fit could be only obtained with two subspectra, as explained in detail elsewhere /12,15/. The first

nonmagnetic component corresponds to room-temperature spectra (Fig. 1) approximated by an asymmetric doublet with all parameters, except δ_1 and the relative area A_1, being fixed in the fit. The second magnetic component was fitted using the algorithm of Blaes et al. /18/, and assuming $\delta_2 = \delta_1$ and fixing the Γ value to the weighted-average of Γ obtained from an asymmetric doublet fit of the spectra in Fig. 1. The parameters /12,15/ obtained from the fit of the x = 0.06 sample are: $\delta_1 = \delta_2 = 0.335(4)$ mm/s, $A_1 = 0.49(1)$, $H_2^{hf} = 26.6(1.3)$ kOe, $QS_2 = -0.340(27)$ mm/s, $\eta_2 = 0.0(1)$, $\alpha_2 = 90(20)°$, and $A_2 = 0.51(1)$. The corresponding parameters for the x = 3 sample are: 0.309(3) mm/s, 0.72(1), 46.8(2.4) kOe, -0.276(99) mm/s, 0.0(1), 90(25)°, and 0.28(1).

The increase of A_1 with x means that for very small Fe concentrations, Fe atoms enter randomly both the nonmagnetic and magnetic class of TM sites. However, for larger concentrations, Fe atoms enter preferentially the nonmagnetic class of TM sites.

It is now well established that, in general, TM atoms either in metals or alloys favour a magnetic state at large volumes and a nonmagnetic state at small volumes /19/. The consequence of disorder in IA, which is manifested by the presence of the $P(\Delta)$ distribution (Fig. 1), is a distribution of volumes, which may lead to the occurrence of nonmagnetic and magnetic class of TM sites /12,15/.

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