High-temperatures magnetism in icosahedral $Al_{52.5}Ge_{22.5}Mn_{25}$ and $Al_{52.5}Ge_{22.5}Mn_{24.85}Fe_{0.15}$

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Magnetization and ^{57}Fe Mössbauer-effect measurements are reported for the magnetically ordered icosahedral alloys $Al_{52.5}Ge_{22.5}Mn_{25}$ and $Al_{52.5}Ge_{22.5}Mn_{24.85}Fe_{0.15}$. The lack of saturation of magnetization suggests a noncollinear magnetic structure. It is shown that transition-metal atoms are distributed among a multiplicity of sites, which is interpreted as evidence for atomic disorder characteristic of icosahedral alloys. The reported and literature data show that the two-site model leads to unphysical Mössbauer parameters. It is shown that ^{57}Fe Mössbauer spectra are due to the simultaneous presence of the electric-quadrupole interaction and the magnetic-dipole interaction, and that the former is significantly stronger than the latter.

I. INTRODUCTION

Until recently, all the icosahedral materials studied exhibited either paramagnetic or diamagnetic properties.[1] The existence of magnetic ordering was convincingly demonstrated for the first time by Tsai *et al.*[2] in single-phase Al-Ge-Mn and Al-Cu-Ge-Mn icosahedral alloys. These alloys have high magnetic ordering temperatures (533 and 467 K for $Al_{52.5}Ge_{22.5}Mn_{25}$ and $Al_{40}Cu_{10}Ge_{25}Mn_{25}$, respectively) and low magnetization (room-temperature values in an applied field of 20 kOe for these two alloys are, respectively, 0.5 and 3.9 emu/g).[2]

Local experimental probes, such as nuclear magnetic resonance (NMR) or Mössbauer spectroscopy (MS), provide useful complementary data on magnetic properties of alloys.[3] This paper reports on preliminary results of magnetization and ^{57}Fe MS measurements of the magnetically ordered $Al_{52.5}Ge_{22.5}Mn_{25}$ icosahedral alloy. For ^{57}Fe MS measurements, an impurity concentration of Fe, enriched to 95% in the ^{57}Fe isotope, was introduced to the alloy by substituting for 0.6 at. % of the $Mn(Al_{52.5}Ge_{22.5}Mn_{24.85}Fe_{0.15})$. We show that ^{57}Fe Mössbauer spectra are due to the simultaneous presence of an electric-quadrupole interaction and a magnetic-dipole interaction, and that the former is significantly stronger than the latter. This conclusion differs from that of a previous ^{57}Fe MS study[4] of the magnetic icosahedral alloy $Al_{40}Cu_7Fe_3Ge_{25}Mn_{25}$, in which it was claimed that the Mössbauer spectrum is due only to a magnetic-dipole interaction.

II. EXPERIMENT

Ingots of composition $Al_{52.5}Ge_{22.5}Mn_{25}$ and $Al_{52.5}Ge_{22.5}Mn_{24.85}Fe_{0.15}$ were prepared by arc melting in an argon atmosphere of high-purity Al, Ge, Mn, and Fe enriched to 95% in a ^{57}Fe isotope. The ingots were metal spun in air by ejecting molten alloy at 1423(10) K through a 0.7-mm-diam orifice in a quartz tube onto the surface of a copper wheel rotating with a tangential velocity of 70(1) m/s.

X-ray-diffraction measurements were performed using a Siemens D500 diffractometer with Cu $K\alpha$ radiation. Magnetization measurements at 4.2 K and in the temperature range 293–617 K were conducted in fields up to 9 kOe using a vibrating-sample magnetometer. ^{57}Fe MS measurements at 4.2 K and room temperature were carried out using a Wissel MSII Mössbauer spectrometer. The surface density of the Mössbauer absorber was 7.0 mg/cm^2.

III. RESULTS AND DISCUSSION

The x-ray-diffraction patterns of the alloys studied indicate high-quality single-phase materials. All lines of the patterns could be indexed[5] to the icosahedral structure, whose "lattice constant" a_R (the edge of the rhombic dodecahedron cells that make up the three-dimensional Penrose tiling[6]) for both alloys is 4.543(2) Å.

Hysteresis curves for $Al_{52.5}Ge_{22.5}Mn_{25}$ and $Al_{52.5}Ge_{22.5}Mn_{24.85}Fe_{0.15}$ measured at room temperature (Fig. 1) and at 4.2 K (Fig. 2) show that even a 0.6-at. % impurity concentration of Fe causes a noticeable, although rather small, increase of magnetization. The values of magnetization measured at 9 kOe, M_9, at room temperature are 0.33 and 0.39 emu/g for $Al_{52.5}Ge_{22.5}Mn_{25}$ and

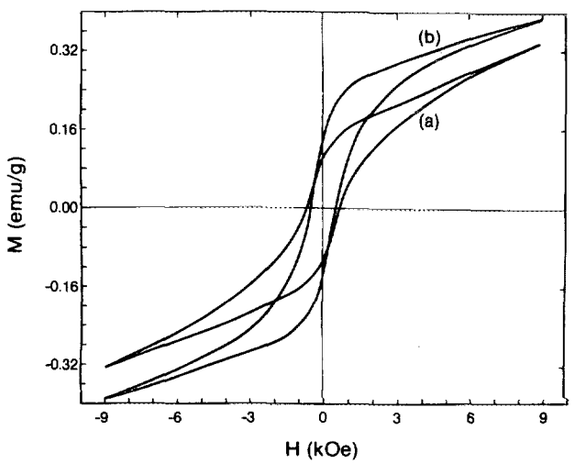

FIG. 1. Room-temperature hysteresis curves for (a) $Al_{52.5}Ge_{22.5}Mn_{25}$ and (b) $Al_{52.5}Ge_{22.5}Mn_{24.85}Fe_{0.15}$.

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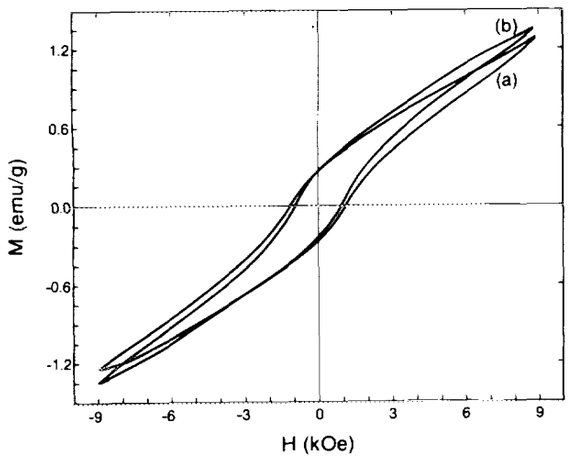

FIG. 2. Hysteresis curves at 4.2 K for (a) $Al_{52.5}Ge_{22.5}Mn_{25}$ and (b) $Al_{52.5}Ge_{22.5}Mn_{24.85}Fe_{0.15}$.

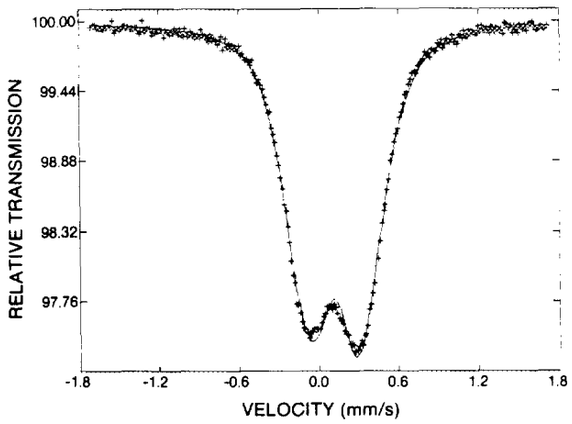

FIG. 3. ^{57}Fe Mössbauer spectrum of icosahedral $Al_{52.5}Ge_{22.5}Mn_{24.85}Fe_{0.15}$ at room temperature fitted (solid line) to a shell model. The velocity scale is relative to the ^{57}Co(Rh) source.

$Al_{52.5}Ge_{22.5}Mn_{24.85}Fe_{0.15}$, respectively. The corresponding values of M_9 at 4.2 K are 1.27 and 1.36 emu/g. Lowering the temperature from 293 to 4.2 K increases M_9 by the factor of 4. It is clear from the hysteresis curves (Figs. 1 and 2) that the icosahedral alloys studied cannot be saturated in a field of 9 kOe. In fact, it has been shown that the room-temperature magnetization cannot be saturated in a field of 20 kOe.[2] This indicates that these alloys may have a noncollinear magnetic structure. The temperature dependence of the magnetization of $Al_{52.5}Ge_{22.5}Mn_{25}$ measured in a field of 4 kOe gives a value of the ordering temperature of 529(5) K, which is in good agreement with the value of 533 K given by Tsai *et al.*[2] We thus conclude that the samples studied are magnetically ordered icosahedral alloys. In order to determine the type of magnetic ordering, high-field magnetization and/or high-field MS measurements are necessary.

The room-temperature ^{57}Fe Mössbauer spectrum of $Al_{52.5}Ge_{22.5}Mn_{24.85}Fe_{0.15}$ measured over a large velocity range $\pm$ 7.5 mm/s does not exhibit a Zeeman pattern as expected for a magnetic sample with an ordering temperature of about 529 K, but instead it consists of two lines characteristic of electric-quadrupole interaction. The room-temperature ^{57}Fe Mössbauer spectrum of this alloy measured over a small velocity range (Fig. 3) clearly demonstrates the absence of lines due to magnetic-dipole interaction. This seemingly surprising result is the consequence of the very small room-temperature magnetization of this sample. If one assumes on the basis of our data and the data of Tsai *et al.*[2] that the room-temperature saturation magnetization of $Al_{52.5}Ge_{22.5}Mn_{25}$ is of the order of 1.0 emu/g, then the magnetic moment per Mn atom is $0.032\mu_B$. One can thus expect a hyperfine magnetic field at the ^{57}Fe nuclei, H_{hf}, estimated from the relation $H_{hf} = a\mu_{Fe}$, with a = 136–142 kOe/μ_B,[3] of about 4.5 kOe. Such a small H_{hf} cannot be detected in the presence of a much larger quadrupole interaction: The value of the magnetic-dipole interaction $g_{3/2}H_{hf} = 0.031$ mm/s, where $g_{3/2}$ is the nuclear g factor for the ^{57}Fe excited state,[7] is more than an order of magnitude smaller than the average quadrupole splitting $\bar{\Delta}$, which for the alloy studied is 0.418 mm/s. This minute magnetic-dipole interaction can only contribute to a slight increase of the width, Γ, of component quadrupole doublets.

The room-temperature ^{57}Fe Mössbauer spectrum of $Al_{52.5}Ge_{22.5}Mn_{24.85}Fe_{0.15}$ was fitted to a shell model, for which the distribution function $P(\Delta) = \Delta^{n-1}/\sigma^n \exp(-\Delta^2/2\sigma^2)$, and by assuming a quadratic correlation between the isomer shift, δ, and Δ ($\delta = \delta_0 + a\Delta + b\Delta^2$). The details of the fitting procedure were described elsewhere.[1,8] The parameters obtained from the fit, which is shown in Fig. 3, $n = 2.053(54)$, $\sigma = 0.329(63)$ mm/s, $\Gamma = 0.256(10)$ mm/s, $\delta_0 = 0.149(5)$ mm/s, $a = -0.137(10)$ (mm/s)$^{-1}$, and $b = 0.114(16)$ (mm/s)$^{-2}$, gave $\chi^2 = 2.36$, $\bar{\Delta} = 0.418(5)$ mm/s, and $\bar{\delta} = 0.122(2)$ mm/s. The linewidth $\Gamma = 0.256$ mm/s is only slightly broader than the linewidth 0.243 mm/s of the inner Zeeman lines of a 6.4-μm Fe foil used for calibration. This broadening reflects the presence of a minute magnetic-dipole interaction, as discussed above.

The shape of the $P(\Delta)$ distribution and the δ-Δ correlation obtained from the fit are shown in Fig. 4. The presence

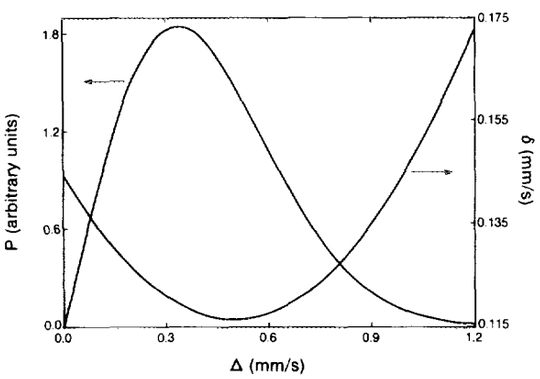

FIG. 4. The distribution function $P(\Delta)$ and the δ-Δ correlation obtained from the fit.

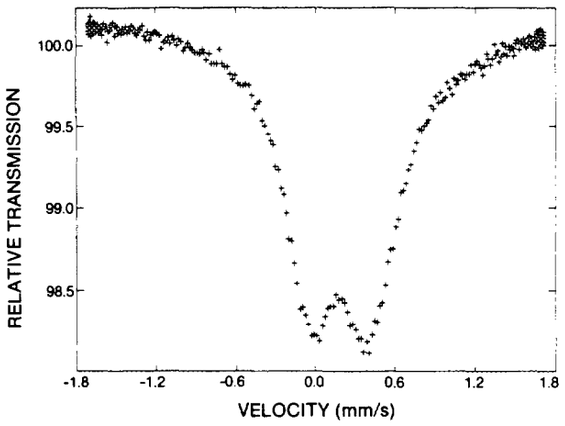

FIG. 5. ^{57}Fe Mössbauer spectrum of icosahedral $Al_{52.5}Ge_{22.5}Mn_{24.85}Fe_{0.15}$ at 4.2 K. The velocity scale is relative to the ^{57}Co(Rh) source at room temperature.

of a distribution of quadrupole splittings is evidence for a continuous distribution of transition-metal sites in the alloy. This reflects the intrinsic disorder present in icosahedral alloys.[1,8,9]

The fit of the experimental spectrum in Fig. 3 to a two-site model[10] gave unphysically broad component lines and a higher value of χ^2. This is in accordance with our previous[1,8] and literature[9] studies, which showed that the Mössbauer data are at variance with such a model.

The two-line-pattern ^{57}Fe Mössbauer spectrum of $Al_{52.5}Ge_{22.5}Mn_{24.85}Fe_{0.15}$ at 4.2 K (Fig. 5) is due to the dominant quadrupole interaction, whose temperature dependence is very small.[1] The presence of a small magnetic-dipole interaction $g_{3/2}H_{hf}$, which at 4.2 K is expected to be of the order of about 0.12 mm/s (assuming the saturation moment of 4 emu/g), is reflected in broadening of the two-line pattern, especially at the wings. The analysis of this spectrum, which is currently underway, must use the full Hamiltonian to calculate the theoretical spectrum since the ratio $R = \bar{\Delta}/g_{3/2}H_{hf}$ (Ref. 7) is larger than 1 and, consequently, the first-order perturbation theory usually used cannot be applied here.

In the previous ^{57}Fe MS study[4] of the magnetic icosahedral alloy $Al_{40}Cu_7Fe_3Ge_{25}Mn_{25}$, the ^{57}Fe Mössbauer spectrum at 110 K was analyzed assuming only the presence of a magnetic-dipole interaction. Our analysis of the room-temperature ^{57}Fe Mössbauer spectrum of this alloy containing a substantially smaller amount of Fe shows that the quadrupole splitting $\bar{\Delta} = 0.422$ mm/s (Ref. 11) is larger than the magnetic-dipole interaction $g_{3/2}H_{hf} = 0.33$ mm/s expected[2,11] for the saturation magnetization of about 10 emu/g. As discussed above, analysis of such a spectrum requires the use of the full Hamiltonian.

ACKNOWLEDGMENTS

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