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Highly symmetric Mn sites in icosahedral Ti-Mn

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We find that the ^{55}Mn NMR linewidth and Knight shift of icosahedral $Ti_{63}Mn_{37}$ (*i*-TiMn) are identical to those of the crystalline phases obtained upon annealing. Comparison of the linewidth in *i*-TiMn and a bcc Ti-Mn solid solution shows that the Mn sites in both phases have a nearly cubic or higher symmetry. These measurements and our analysis provide strong evidence for a large density of structurally ordered, highly symmetric sites in an icosahedral alloy and demonstrate that a high degree of structural disorder is not an intrinsic property of the icosahedral phase.

It has been five years since the first icosahedral phase (*i* phase) was discovered by Shechtman *et al.* in an Al-Mn alloy.[1] Remarkably, the exact structure and the atom locations for that phase or any subsequently discovered *i* phase are still unknown. The local atomic configuration of the *i* phase is often assumed to be similar to that of related complex crystal phases containing many atoms per unit cell.[2] While diffraction studies by x ray and electron microscopy have been useful in deciding between competing structural models (e.g., quasicrystal[3] versus icosahedral glass[4]), they are of limited use in determining the local site environments of the atoms. Local probes such as nuclear magnetic resonance (NMR), Mössbauer spectroscopy, and extended x-ray absorption fine structure (EXAFS) provide information complementary to diffraction studies, which can more effectively guide structural modeling. Most previous studies in *i*-phase systems with these local probes have led to similar results: the atoms sit in a broad distribution of sites of relatively low symmetry. This has led to the suggestion that a high degree of atomic structural disorder is an intrinsic property of the *i* phase.

There have been several NMR measurements on the *i* phase and related crystal phases in Al-Mn-based alloys.[5-8] The linewidths in the *i* phase are much greater than in the crystalline phases. Other studies have examined the local structure using Mössbauer spectroscopy[9-12] and EXAFS.[13-16] While some of the EXAFS and Mössbauer data have been fitted by assuming two distinct sites for the Mn, other investigators have been forced to conclude that there exists a broad distribution of Mn sites of low symmetry. Recent Mössbauer measurements of the *i* phase in $Ti_{56}Ni_{28-x}Fe_xSi_{16}$ ($x \leq 7.5$), suggest that the Fe atoms occupy highly symmetric sites;[12] however, no information was available for most of the atomic sites. Similarly, recent NMR measurements[17] in *i*-phase Al-Li-Cu suggest that the Li atoms occupy fairly symmetric sites, but no quantitative evaluation of the site symmetry was presented.

Here we present the first NMR measurements of Mn in the recently reported *i* phase in rapidly quenched Ti-Mn alloys.[18] These are compared with NMR measurements made by us of the β-Ti phase (a bcc solid solution of Ti and Mn) and of complex crystalline phases obtained upon annealing the *i* phase. Our model calculations for quadrupolar widths show that the overwhelming majority of Mn sit in sites of nearly cubic or higher symmetry. These results are significant in that the Mn atoms constitute both a strong probe of site symmetry and are a major alloy constituent.

Ribbons of *i* phase Ti-Mn were prepared by melt spinning onto a copper disk in an argon atmosphere.[19] X-ray powder diffraction and transmission electron microscopy (TEM) studies of the as-quenched samples confirmed that they were primarily *i* phase, containing less than 15% of β-Ti. Annealing at 1000 °C completely transformed the sample to a phase mixture of at least two unidentified complex crystal phases.[19] Energy dispersive x-ray spectroscopy measurements in TEM gave a composition of $Ti_{60}Mn_{37}Si_3$ for the *i* phase, $Ti_{68}Mn_{29}Si_3$ for one crystalline phase, and $Ti_{58}Mn_{39}Si_3$ for the other crystalline phase; the β-Ti contained approximately 26% Mn, the solubility limit near the eutectic temperature. The silicon entered the melt by reaction with the fused silica crucible. A ribbon of β-Ti was also made by rapidly quenching a $Ti_{74}Mn_{26}$ melt.

Spectra of ^{55}Mn were obtained with the field-swept spin-echo method. The ^{55}Mn spectrum of *i*-TiMn at 20.38 MHz and 4.2 K appears in Fig. 1(a). The narrower resonance is the central $m = -\frac{1}{2} \to \frac{1}{2}$ transition of the spin-$\frac{5}{2}$ nucleus. A selection rule prohibits first-order quadrupole broadening of the central transition. The broader resonance is due to the other transitions (satellites) which are first-order quadrupole broadened. Though not apparent from Fig. 1(a), a wider field sweep shows that the satellites have nearly zero amplitude at the extremes of Fig. 1(a). The ^{55}Mn line of a ribbon crystallized by annealing for 30 min at 1000 °C is presented in Fig. 1(b). The linewidths and positions (i.e., Knight shifts) are identical to those obtained for the *i*-TiMn.

In Fig. 1(c), we present the ^{55}Mn spectrum of the solid solution, β-Ti. The line is somewhat narrower than in *i*-TiMn. A Knight shift of the position of the line relative to *i*-TiMn is also present. For second-order quadrupole broadening of a central $(-\frac{1}{2}, \frac{1}{2})$ transition, the width varies as the square of the quadrupole interaction. Thus the narrower central line of β-Ti indicates that the quadrupole interactions in β-Ti are $\approx 25\%$ smaller than in *i*-TiMn. This variation is in reasonable agreement with the widths of the first-order broadened satellites in Figs. 1(a) and 1(c).

The dominant source of line broadening in the Ti-Mn samples is quadrupolar (see field dependence experiments below). Quadrupole interactions as well as the Knight shift reflect mainly the nearest- and next-nearest-neighbor environments.[20] Thus, the observation of identical NMR lines in *i*-TiMn and in the crystallized sample demonstrates that the local environments of the Mn atoms are very similar in the two materials. This conclusion is supported by our electron diffraction studies which showed that the modulations of the diffraction intensities for the complex crystalline structures are almost identical to those of the *i* phase.[19] These results support the notion that the *i* phase and the crystals are built from similar "building blocks" that are arranged differently.

Second-order quadrupole broadening of a central transition is inversely proportional to the applied field,[20] or equivalently, to the resonance frequency. On the other hand, a distribution of Knight shifts produces a broadening proportional to the field. A comparison of Figs. 2(a) and 2(b) shows that the 10.19-MHz resonance is broader than at 20.38 MHz. At 10.19 MHz the amplitude of the satellite transitions relative to the central transition is increased, confirming the broadening of the central transition. The central and satellite transitions are less clearly distinguished at 10.19 MHz, making it difficult to quantitatively establish the width of the central feature. Since the central transition broadens upon decreasing the field and frequency, the second-order quadrupole broadening exceeds the broadening from Knight-shift distributions in *i*-TiMn at these frequencies.

The 20.38-MHz resonances of ^{55}Mn in *i*-TiMn at 4.2 and 77 K are compared in Figs. 2(b) and 2(c), respectively. The lower signal-to-noise ratio at 77 K is apparent and reflects the Curie nuclear susceptibility. The peak positions are the same and the 4.2-K linewidth is only slightly larger, the change being at the limit of our precision. The 300-K spectrum (not shown) also has the same linewidth,

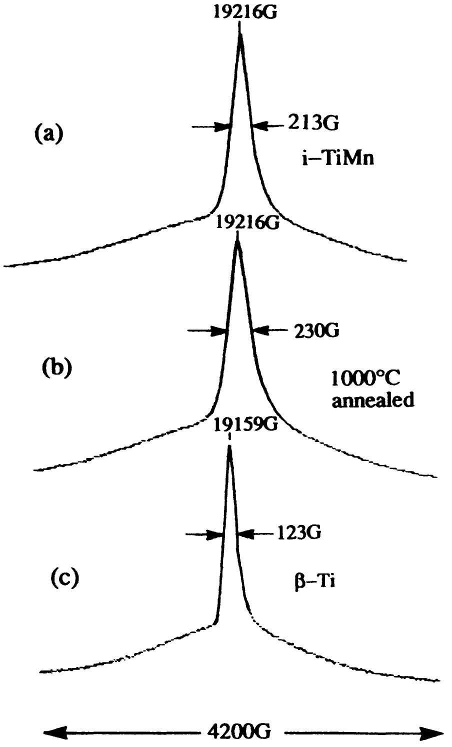

FIG. 1. Comparison of ^{55}Mn spectra of the Ti-Mn samples at 20.38 MHz and 4.2 K. (a) Icosahedral Ti-Mn. (b) Polycrystalline result of 1000 °C anneal. (c) β-Ti, a bcc solid solution of Ti and Mn.

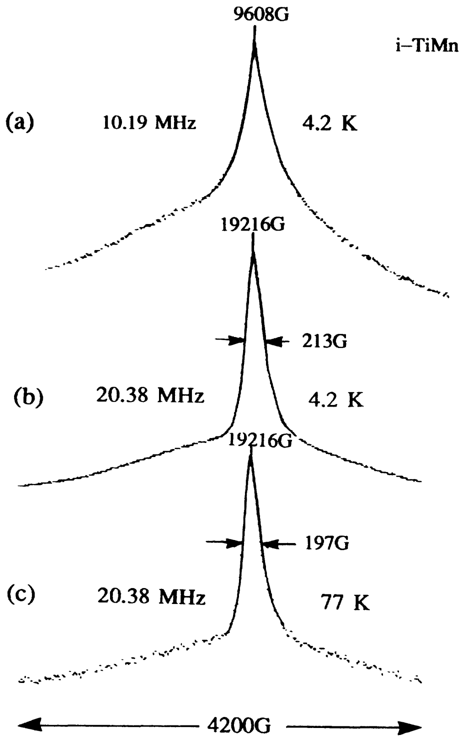

FIG. 2. Comparison of ^{55}Mn spectra of icosahedral Ti-Mn at different frequencies and temperatures.

although the poor signal-to-noise ratio creates ±25% error limits on the linewidth. The absence of appreciable linewidth changes with temperature down to 4.2 K indicates that *i*-TiMn has few local moments, if any. In contrast, local moments are present in *i*-AlMn.[6] Our band-structure calculations[21] for hypothetical Ti_3Mn and Al_3Mn compounds in the Fe_3Al and Cu_3Au structures confirm this difference. These calculations indicate that if local moments form in Ti_3Mn, they are small ($\leq 0.1\mu_B$), while large local moments of magnitude $1\mu_B$ or more form in Al_3Mn.

The Knight shift of *i*-TiMn is +0.5% paramagnetic (higher NMR frequency at fixed field compared to the bare nucleus). The shift of β-Ti is +0.8%. The difference between β-Ti and *i*-TiMn may be due in part to the different Mn concentrations (26% for β and 37% for *i* phase). The small distribution of Knight shifts (most of the central width is second-order quadrupolar) indicates that the Mn sites in *i*-TiMn have similar electronic environments.

It is useful to compare the ^{55}Mn resonance in *i*-TiMn with the ^{55}Mn and ^{27}Al resonances of *i*-AlMn, both near 20 MHz. The ^{55}Mn line of *i*-AlMn is so broad that it appears only as an asymmetry in the overlapping ^{27}Al resonance.[5,6] The ^{55}Mn spectrum has been deconvolved[5,6] and the resonance is much broader (≈ 800 G or more) than that observed here. By chance, the ^{27}Al line in *i*-AlMn has a central transition width similar to that of ^{55}Mn in *i*-TiMn; the satellites are also of similar widths.[5] The nuclear quadrupole moment of ^{55}Mn exceeds that of ^{27}Al by a factor of 4 and the Mn Sternheimer factor[22] is about 8, while that of Al is about 2. Since the quadrupole coupling strength is proportional to the product of the nuclear quadrupole moment, the Sternheimer factor, and the electric field gradient (EFG), the EFG's at Mn sites in *i*-TiMn must be about 16 times smaller than at Al sites in *i*-AlMn.

To crudely estimate the degree of site asymmetry, we assume superposed model atomic 4*s* charge densities, obtained by fitting to Hartree-Fock-Slater densities.[23] The electronic charge is neutralized by a point charge at the origin. We assume a typical transition metal valence of ≈ 1.5. From this model, chemical disorder with no accompanying structural disorder would produce linewidths about 2 orders of magnitude less than those observed. However, chemical disorder always leads to some structural disorder. For metals one can expect strains about half as large as one would get by assuming that all interatomic spacings depend only on the pair and not on the environment ($\approx 2\%$ for Ti-Mn). Our model agrees with the experimental data if we assume typical strains of 0.02 and 0.03 for the β-TiMn (Ref. 24) and *i*-TiMn, respectively. Thus the structural disorder associated with the chemical disorder in *i*-TiMn can explain the linewidth.

In summary, we have presented the first NMR measurements on the icosahedral phase and related crystalline phases in rapidly quenched Ti-Mn alloys. The spectra for *i*-TiMn and its crystalline transformation products are very similar. This suggests that the local site symmetries for the Mn are similar in the *i* phase and the crystalline phases and strongly supports the notion of a common building block. The ^{55}Mn lines for this *i* phase are much narrower than those previously obtained from the *i* phase in rapidly quenched Al-Mn alloys. Our experimental measurements combined with our model calculations provide compelling evidence for highly symmetric sites for a major constituent of an icosahedral alloy. Our results demonstrate that a high degree of atomic structural disorder is not an intrinsic property of an icosahedral phase.

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[1] D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984).

[2] V. Elser and C. L. Henley, Phys. Rev. Lett. **55**, 2883 (1985).

[3] D. Levine and P. J. Steinhardt, Phys. Rev. Lett. **53**, 2477 (1984); Phys. Rev. B **34**, 596 (1986).

[4] P. W. Stephens and A. I. Goldman, Phys. Rev. Lett. **56**, 1168 (1986); **56**, 2331 (1986).

[5] W. W. Warren, Jr., H. S. Chen, and J. J. Hauser, Phys. Rev. B **32**, 7614 (1985).

[6] W. W. Warren, Jr., H. S. Chen, and G. P. Espinosa, Phys. Rev. B **34**, 4902 (1986).

[7] M. Rubinstein, G. H. Stauss, T. E. Phillips, K. Moorjani, and L. H. Bennett, J. Mater. Res. **1**, 243 (1986).

[8] K. R. Carduner, B. H. Suits, J. A. Diverdi, M. D. Murphy, and D. White, J. Mater. Res. **2**, 431 (1987).

[9] P. J. Schurer, B. Koopmans, and F. van der Woude, Phys. Rev. B **37**, 507 (1988).

[10] R. A. Dunlap, D. W. Lawther, and D. J. Lloyd, Phys. Rev. B **38**, 3649 (1988).

[11] Z. M. Stadnik and G. Stroink, Phys. Rev. B **38**, 10447 (1988).

[12] R. A. Dunlap, M. E. McHenry, R. C. O'Handley, V. Srinivas, and D. Bahadur, Phys. Rev. B **39**, 1942 (1989).

[13] A. Sadoc, A. M. Flank, P. Lagarde, P. Sainfort, and R. Bellissent, J. Phys. (Paris) **47**, 873 (1986).

[14] Y. Ma and E. A. Stern, Phys. Rev. B **35**, 2678 (1987).

[15] A. Sadoc, J. Non-Cryst. Solids **106**, 166 (1988).

[16] A. Sadoc, A. M. Flank, and P. Lagarde, Philos. Mag. B **57**, 399 (1988).

[17] C. Lee, D. White, B. H. Suits, P. A. Bancel, and P. A. Heiney, Phys. Rev. B **37**, 9053 (1988).

[18] K. F. Kelton, P. C. Gibbons, and P. N. Sabes, Phys. Rev. B **38**, 7810 (1988).

[19] J. C. Holzer, K. F. Kelton, L. L. Levine, and P. C. Gibbons, Scr. Metall. **23**, 691 (1989).

[20] See, for example, C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, New York, 1978).

[21] The calculations were performed using the augmented-spherical-wave (ASW) method, described in A. R. Williams, J. Kübler, and C. D. Gelatt, Phys. Rev. B **19**, 6094 (1979). The implementation is the same as in that reference, except that

equal ASW sphere radii are used for all sites.

[22] R. M. Sternheimer, Phys. Rev. **146**, 140 (1966); F. W. Langheff and R. P. Hurst, Phys. Rev. **139A**, 1415 (1965).

[23] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, 1963).

[24] The additional presence of the ω phase in β-Ti, revealed by TEM diffraction studies, complicates this argument. Undistorted ω phase is a hexagonal phase that appears in many Ti-based solid solutions and results from a displacement transformation along the $\langle 111 \rangle$ of the bcc unit cell. On the basis of TEM studies, however, we find that most of the sample is bcc. As further support, the central transition of the spectrum in Fig. 1(c) does not appear to have two components.