Magnetism and the observation of NMR lines in hexagonal Al_4Mn and icosahedral Al-Mn alloys

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Previous measurements of the magnetic susceptibility and the intensity of the ^{55}Mn NMR line in a number of periodic and quasiperiodic (i.e., icosahedral) Al-Mn and Al-Mn-Si alloys suggested some correlation, in that the ^{55}Mn line intensity decreases as the magnetic susceptibility increases. This correlation had led to the tentative conclusion that the reduction of the ^{55}Mn line intensity is due to the magnetism, and that the "magnetic" Mn atoms are not seen in the NMR. We have found that the above correlation breaks down in a very substantial way for hexagonal Al_4Mn which (i) shows a *small* magnetic susceptibility, and (ii) no observable ^{55}Mn line. Thus the reduction in intensity in the ^{55}Mn NMR line in the icosahedral phase is not necessarily due to its magnetism but may have its origin in another line broadening mechanism.

BACKGROUND

Since the remarkable discovery of Shechtmanite,[1] a rapidly quenched Al-Mn alloy with icosahedral symmetry, a large amount of work has been directed to (1) understanding the structure and (2) determining the physical properties. An important question is what unique electronic and magnetic properties, if any, are associated with the quasiperiodicity. A number of investigators[2–4] have suggested, for example, that the icosahedral phase will have an anomalously high density of states at the Fermi energy. Resistivity measurements are said[4] to be in agreement with this. On the other hand, low-temperature specific heat measurements[5] do not confirm a large enhancement of the density of states.

There have been several reports[4–9] of magnetic measurements in Shechtmanite. Hauser *et al.*[6] found that the icosahedral alloys of the type $(Al_{1-y}Si_y)_{1-x}Mn_x$ ($x = 0.14$–0.22, $y = 0$–0.06) exhibit strong Curie–Weiss paramagnetism implying a magnetic moment, and in low fields, spin-glass behavior. They also found that the temperature dependence, and hence the moment, increases with increasing Mn concentration. Similar behavior was also reported[6] in amorphous alloys with the same compositions. Assuming that the magnetic moment is equally distributed on all of the Mn sites, they obtained an effective moment of 1–$1.5\mu_B$ on each Mn. In contrast, the periodic crystalline phases they studied,[6,7] i.e., orthorhombic Al_6Mn and cubic $Al_{73}Si_{10}Mn_{17}$, are weak paramagnets. They[6] also noted that the amorphous phase displayed ferromagnetism ($T_C = 110$ K) for high Si concentrations. Yasuoka *et al.*[9] obtained moment values in agreement with Hauser *et al.*[6] In contrast, a French group[8] has found only a very small moment, $10^{-2}\mu_B$, on the Mn. Machado *et al.*[5] found a magnetic term in their low-temperature specific heat measurements on icosahedral $Al_{80}Mn_{20}$. They also measured the magnetic susceptibility and found that, if it is assumed that all of the Mn atoms have moments, the average moment is $1.12\mu_B$, in agreement with Hauser *et al.*[6] However, they claim that the data is better interpreted by assigning a localized moment of $9.9\mu_B$ for approximately one in every 80 Mn atoms.

Nuclear magnetic resonance (NMR) measurements in Shechtmanite, in another Al-Mn quasiperiodic crystal (the T phase) and in Al-Mn periodic crystals have been reported[9–13] in the literature. Warren *et al.*[10] noted an interesting correlation between the increase in the effective magnetic moment for increasing Mn concentrations, found by Hauser *et al.*[6] in the icosahedral alloys, and a corresponding decrease in the intensity of the ^{55}Mn NMR line. On the basis of experience with the behavior of hyperfine fields and susceptibility in $3d$ metals, they concluded that the observed ^{55}Mn NMR signal is due to Mn sites which do not contribute much to the bulk paramagnetism. We are in complete agreement with this conclusion. They[10] also concluded that the remaining Mn sites must carry local moments which are larger than the average moments obtained by assuming that all Mn atoms contribute equally to the magnetization. This is a reasonable conclusion. However, we then found an experimental result which is startling if this conclusion is accepted.

EXPERIMENTAL RESULTS

We measured the NMR of the hexagonal Al_4Mn phase. (This phase has lattice constants[11] $a = 2.835$ nm and $c = 1.236$ nm.) We found no observable ^{55}Mn line. Our sensitivity was such that we would have been able to observe any line with maximum amplitude of at least 5% of the line in the much more magnetic icosahedral Al-Mn-Si alloy. Based on the conclusions of Warren *et al.*,[10] we then would expect that this Al_4Mn crystal would be quite magnetic. We measured its magnetic susceptibility using a SQUID magnetometer. The result, shown in Fig. 1, is that it is considerably less magnetic than an icosahedral Al-Mn-Si alloy whose ^{55}Mn resonance[12] we could easily observe! (Since we made this

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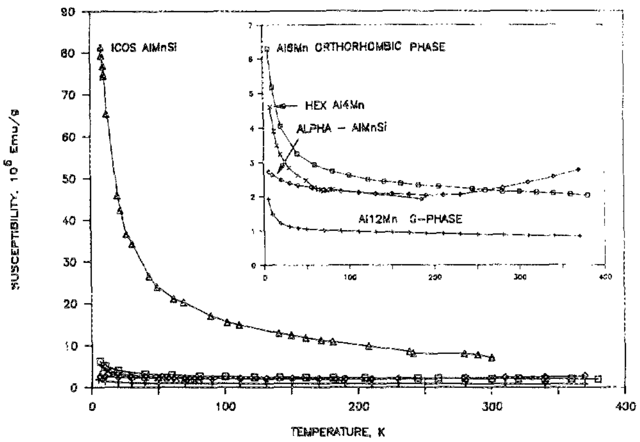

FIG. 1. Susceptibility of a icosahedral Al-Mn-Si alloy and of hexagonal Al_4Mn, cubic $Al_{12}Mn$ (the so-called "*G*" phase), cubic αAl-Mn-Si, and orthorhombic Al_6Mn, as a function of temperature. Data taken at 1.5 T in a SQUID magnetometer.

measurement, we have learned of a susceptibility measurement by Yasuoka *et al.*[9] on hexagonal Al_4Mn, which also shows considerably lower magnetism than in the icosahedral phase.) Our susceptibility result for the icosahedral phase (Fig. 1) is in agreement with other reported[5] measurements. Also shown in Fig. 1 are susceptibility measurements on three other periodic crystals in the Al-Mn and Al-Mn-Si alloy systems. These results will be discussed more completely elsewhere.

DISCUSSION

The magnetic susceptibility and the intensity of the ^{55}Mn NMR line in a number of periodic and quasiperiodic (i.e., icosahedral) Al-Mn and Al-Mn-Si alloys have been measured and there is, as previously reported,[10] some correlation between these two measurements: the ^{55}Mn line intensity decreases as the magnetic susceptibility increases, in most cases. This correlation had led[10] to the tentative conclusion that the reduction of the ^{55}Mn line intensity is due to the magnetism, and that the "magnetic" Mn atoms are not seen in the NMR.

In the present work, we have found that the above correlation breaks down for hexagonal Al_4Mn which is only weakly magnetic (Fig. 1) but has no observable ^{55}Mn NMR line. Since we cannot explain its absence by the explanation offered by Warren *et al.*[10] for the reduction of intensity in the ^{55}Mn resonance of the icosahedral alloy, namely, that Mn possesses a magnetic moment which broadens the line, we have to seek an explanation elsewhere. It may be that the Mn in hexagonal Al_4Mn has a very large quadrupole splitting (with a ν_q value of several MHz), or that it occupies several different sites with widely different Knight shifts. Further experiments with alloy substitutions at the Mn site may help to clear up the matter. Of perhaps more immediate importance, the results on hexagonal Al_4Mn suggest that the reduction in intensity in the ^{55}Mn NMR line in the icosahedral phase is not necessarily due to its magnetism but may also have its origin in another line broadening mechanism. If this is so, it is possible to *speculate* that the magnetism observed in the susceptibility measurements is not observed in the NMR spectra. This could be true if the Machado *et al.*[5] conclusion is correct: the magnetism per atom is large, but only a few percent of the atoms are magnetic. In turn, this is consistent with the NMR samples not being homogeneous. The "magnetic" Mn could be clusters in the icosahedral phase, or could represent another phase. We already know that there is some fcc Al phase present,[12] but this contains only isolated Mn atoms and is not likely magnetic. Perhaps there is a magnetic "interface phase" present between the icosahedral phase and the fcc Al phase. A metastable ferromagnetic phase[14] exists in the binary Al-Mn alloy system near the equiatomic composition (produced on quenching from the ϵAl-Mn high-temperature stable phase). The magnetic measurements are not consistent with this phase being present in the icosahedral alloys, but it would not be surprising if a precipitate or an interface region enhanced in Mn contents above the 20 at. % level could produce the enhanced paramagnetism observed. Then the magnetic properties are those to be expected from Al-Mn alloys, and are not peculiar to the icosahedral phase.

ACKNOWLEDGMENT

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