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The aim of this program was to understand the consequences of long-range and short-range icosahedral order on magnetism in quasicrystalline alloys. At the time of its outset, there were no known or suspected magnetic quasicrystals. We set out to make some and succeeded. We later showed these alloys to be concentrated spin glass. Along the way we made new quasicrystals in the TiNi(Fe)Si system that showed no quadrupole splitting in their Mossbauer spectrum. This strongly suggests high site symmetry for the iron absorbers. We did extensive work on transition-metal-sibstituted Mn-Al-Si quasicrystals gaining insight into the interplay between site selection, site volume and magnetic moment formation.

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Icosahedral and other quasicrystal phases in magnetic alloy systems

FINAL REPORT

R.C. O'Handley

September 12, 1990

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RESEARCH SUMMARY

Background

Symmetry arguments suggest, and electronic structure calculations support the notion, that a transition metal atom in an icosahedral (I_h) environment should show an enhanced magnetic moment. This program was aimed at methodically moving toward the development of magnetic quasicrystals (QC's) from the then known Al-Mn-Si QC's and other weakly magnetic icosahedral systems.

While most sites in an icosahedral QC are not of high symmetry, preferential occupation of the icosahedral site by a particular transition metal species such as Fe (e.g. AlMn(Fe)Si) would enhance the Fe moment. This should be detectable in the magnetic susceptibility and Mossbauer spectrum.

Our early experimental work confirmed that Mn itself shows a larger local moment in quasicrystalline alloys (1.2 - 1.5 μ_B/Mn, average) than in related crystalline structures (0 - 0.5 μ_B/Mn), possibly because some of the Mn atoms them occupy the I_h site. The need existed to 1) find QC's that more readily admitted potentially magnetic atoms to high symmetry sites and 2) to develop quasicrystals with higher transition metal content if ferromagnetism were to be observed.

Ti_2Ni based Q.C.'s

The Ti_2Ni crystal structure has Ni sites of nearly icosahedral symmetry. We showed that the mixed quasicrystal/crystal system explored earlier by Kuo, namely rapidly solidified $(VTi)_2Ni$, could be made to give high quality QC's by the addition of Si: $Ti_{56}Ni_{28}Si_{16}$. However, the Ni moment in this system is quenched (See Table I, below) presumably because its low lying atomic d-states are filled upon alloying. We do not believe the moment is suppressed due to strong hybridization with the more itinerant Ti d band because of the incompatibility of d with I_h symmetry and because a tight binding or configuration model should be even more valid for Ni than for Mn.

We looked for stronger magnetism by making earlier transition metal substitutions for Ni. We first found that $Ti_{56}Ni_{28-x}Fe_xSi_{16}$ gives excellent single-phase, quasicrystalline samples. More importantly, their Mossbauer spectra show a narrow singlet indicating Fe occupies sites of cubic or higher symmetry. In contrast, our Mossbauer studies of AlMn(Fe)Si QC's and amorphous or crystalline Ti_2Ni or TiNiFe alloys invariably showed a significant quadrupole splitting. So this was an amazing result (Fig. 1). The quasicrystal structure contains no cubic sites, only the icosahedral sites and several sites of symmetry lower than cubic. At such high symmetry sites a transition metal atom should have a narrow d-band (unsplit by the crystal field) and may, therefore, develop a large moment if its d bands remain partially filled.

The T moments we observed in the $Ti_{56}Ni_{28-x}T_xSi_{16}$ system are compared in the table below with the moments of these species in Al-Mn-Si.

TABLE I

Transition metal moments at low concentrations in quasicrystal hosts.

HOST	T =	Mn	Fe	Co	Ni
$Ti_{56}Ni_{28-x}T_xSi_{16}$		0.6	0.2	-	0.06
$Al_{92-x}T_xSi_8$		0.4*	0.0	0.0	0.0

*$\mu_{Mn} = 1.2\ \mu_B$ for x close to 0.2

These lower-than-optimum moments in the TiNi base QC's may be the result of partial d-band filling by valence charge from Ti. Electronegativity increases from left to right in the 3d series.

AlMn(VCrFe)-Si

At an early stage we studied the Al(FeCr)Si system to investigate whether the Mn moment in AlMnSi QC's is a local moment due to the unique electronic configuration of Mn ($3d^5$) or can be explained better in terms of a band model with emphasis on the average d electron concentration (Fe and Cr straddle Mn in the 3d series and therefore have the same average d-electron concentration as Mn). The absence of a significant moment in Al(FeCr)Si confirms the local moment picture.

Our extensive studies on Al-Mn(VCrFe)-Si QC's indicated that the condition more favorable to magnetic moment formation is a small ratio of transition metal atom volume to site volume. We therefore explored ways of expanding the Al-Si network by replacing Si with Ge.

Al-(MnCr)-Ge Quasicrystals

Two families of Ge-containing QC's were made by melt spinning $Al_{65}Cr_{20-x}Mn_xGe_{15}$ ($0 \le x \le 20$) and $Al_{60}Mn_{20}Ge_{20}$. The important results are

1) that the effective paramagnetic moment per Mn atom has been raised to 2.1 μ_B/Mn compared to a maximum of 1.2 μ_B/Mn in Si containing Q.C.'s. This is larger than the moment observed in any other Q.C
2) for the first time a quasicrystal has been made in which Cr shows a significant paramagnetic moment, 0.45 μ_B/Cr. The higher moments in these new Q.C.'s are believed to be due to an expansion of the quasilattice brought about by replacing Si with Ge (covalent radius increases from 1.1 Å to 1.22 Å).

The non-monotonic compositional dependence of the susceptibility across the $Al_{65}Cr_{20-x}Mn_xGe_{15}$ ($0 \le x \le 20$) series suggests at least two classes of magnetic sites in these structures rather than two constant moments, Mn and Cr, combining by a lever rule to give a mean paramagnetic moment.

Spin glass behavior was observed below 8 K in icosahedral $Al_{65}Mn_{20}Ge_{15}$ suggesting either a random local anisotropy or competing ferro-and antiferromagnetic exchange interactions due to a distribution of environments available to the magnetic species. The decay of magnetization in the spin glass state was found to be logarithmic in time and could be analyzed to indicate a mean activation barrier of 6.8 meV for re-orientation of the moments by a field against the local random

anisotropy. In such a model 6.8 meV corresponds to a giant local anisotropy energy density of order 3×10^8 erg/cm^3.

Si-rich Al-Mn-Si Q.C.'s

Amorphous Al-Mn-Si alloys containing 25-30% Si were found by Hauser to be ferromagnetic with T_c = 110 K. By melt spinning several of these compositions at slower wheel speeds we fabricated single-phase quasicrystals with no x-ray evidence of amorphous or crystalline structures present. The magnetization vs. temperature and field is shown in Fig. 2. The results suggest ferromagnetic behavior with a very weak moment.

Also two alloys enriched in Si, $Al_{50}Mn_{20}Si_{30}$ and $Al_{55}Mn_{20}Si_{25}$, were prepared by melt spinning and found to be fully amorphous. When annealed below their crystallization temperatures ($T_x \sim 650$ K) they transform to a single icosahedral phase having a quasilattice constant of 0.458 nm, only 0.65% less than that of $Al_{74}Mn_{20}Si_6$. Both the amorphous and Q.C. phases are ferromagnetic with $T_c \sim 120$ K and spontaneous magnetization of about 0.2 emu/g. Appreciable high-field susceptibility coexists with the spontaneous moment only in the Q.C.'s. The Q.C. paramagnetic moment is 0.24 to 0.32 μ_B/Mn, about 25% of the paramagnetic moment in $Al_{74}Mn_{20}Si_6$ Q.C.'s.

Table II Magnetic properties of amorphous and quasicrystalline Si-rich Al-Mn-Si alloys. Average values for the Si_{25} and Si_{30} compositions are given.

	Amorphous	Quasicrystaline
T_c (K)	108	113
n_o(ferro) μ_B/Mn	0.0026	0.0061
μ_p (para) μ_B/Mn	~ 0	0.28

A major question to be addressed was the possibility that the ferromagnetism was due to a small amount of magnetic impurity: a magnetic Mn phase or simply traces of Fe. While this possibility cannot be decisively ruled out, several facts make it extremely unlikely. 1) It is improbable that such a small amount of a magnetic phase would remain unchanged during the annealing yet we see the same ferromagnetic moment in amorphous and Q.C. samples. 2) Trace amounts of Fe would show T_c > 1000 K if precipitated as a-Fe and lower T_c if alloyed. Again it seems likely that the equilibrium alloy composition (T_c of annealed QC) would be quite different from that of the non-equilibrium amorphous alloy. 3) Finally, and most convincingly we feel, FMR studies have shown the strongest resonance signal, that due to the majority, Q.C. phase, to vanish at T_c = 115 K, identifying it (and not some impurity phase) as the ferromagnetic component.

We examined closely one well-documented crystalline phase, AlMnFe. It is instructive to compare the ferromagnetic properties of icosahedral Al-Mn-(SiGe) with those of the related equiatomic crystalline AlMnGe which has the tetragonal Cu_2Sb structure.[2] The table below shows that the larger Mn-Mn spacing r_{Mn-Mn} in the crystal correlates with the stronger magnetism observed there. We have not yet made a feromagnetic AlMnGe quasicrystal so the effective *paramagnetic* moment per Mn atom p_{Mn} is reported. The trends shown in the table are consistent with a

simple Bethe-Slater picture of distance-dependent-exchange. Also, the data rule out the possibility that the ferromagnetic is due to AlMnGe precipitates because of the T_c's.

	$Al_{37}Mn_{30}Si_{33}$	$Al_{65}Mn_{20}Ge_{15}$	AMnGe
Structure	icos.	icos	Cu_2Sb
r_{Mn-Mn} (Å)	2.59		2.77
T_c(K)	107	-	518
μ_{Mn} (μ_B)	< 0.1	-	1.7
p_{Mn} (μ_B)	-	2.1	2.9

We used Mossbauer effect spectroscopy to study the ferromagnetic quasicrystals $Al_{40}Mn_{25}Cu_{10-x}Fe_xGe_{25}$ reported by Tsai et al. The iron hyperfine field is much smaller than that of metallic α-Fe (15-20 kOe vs 250 kOe), it vanishes at T_c = 465 K as it should and it is relatively insensitive to x below T_c.

Possibly the most important advance on this project came in the form of a much better understanding of the nature of the magnetism in these so-called ferromagnetic quasicrystals. In a word, what we made are actually re-entrant ferromagnetic quasicrystals, i.e. they revert to spin glass behavior below $T_g << T_c$. This explains the low magnetic moment, consistent T_c and large high-field susceptibility.

A careful and complete set of M(H,T) data was taken on icosahedral $Al_{37}Mn_{30}Si_{33}$. While T_c = 120 K for this material, the magnetization below T_c is very weak, M (5 kOe, 5 K) = 1.4 emu/g, and is strongly field dependent (Fig. 3). Arrott plots of this data, Fig. 4, tell the true story:

the spontaneous magnetization (y intercept) is zero below T_c and the initial susceptibility (inverse of x intercept) approaches infinity even below T_c. Thus the observation of what resembled weak ferromagnetism was shown to be a concentrated spin glass state. We confirmed this with time dependent susceptibility studies. Moreover, we located this reentrant ferromagnetic quasicrystal as well as our earlier paramagnetic/dilute spin glass QC and Masumoto's high T_c ferromagnetic QC on the Selimeyer-Nafis phase diagram (Fig. 5). Here $t = T/J_o$ and $d = D/J_o$ are the reduced temperature and random anisotropy, normalized with respect to the mean exchange energy J_o. Exchange fluctuations were assumed to be negligible in these systems. Located on the figure are three representative QC's: $Al_{74}Mn_{21}Si_5$ which is paramagnetic with a transition to spin glass behavior at low T; $Al_{37}Mn_{10}Si_{33}$ (our result) which has T_c = 120 K and Tg = 8 K; and $Al_{40}Mn_{25}Ge_{25}Cu_{10}$ which has T_c = 500 K. While there is no reported spin glass behavior in the last mentioned Q.C., the saturation magnetization of 2 emu/g and strong field-dependent magnetization suggests that a considerable random anisotropy tends to frustrate the magnetic ordering in this composition also.

From Fig. 5 it is clear that the path to stronger ferromagnetic Q.C.'s lies in reducing the random anisotropy D and increasing the exchange J_o. The major question now being asked is whether the randomness in the anisotropy is intrinsic to the QC state or is simply a result of quenching these metastable Q.C.'s.

Conclusion

It appears to me that without a major breakthrough such as discovery of an entirely new Q.C. system, the pursuit of useful magnetic properties in icosahedral Q.C.'s will be a slow process. The local random anisotropy appears to be so strong that it will frustrate the development of any significant average magnetization.

My judgement at this time is that our efforts would be much better spent in more fertile fields such as surface or thin film magnetism.

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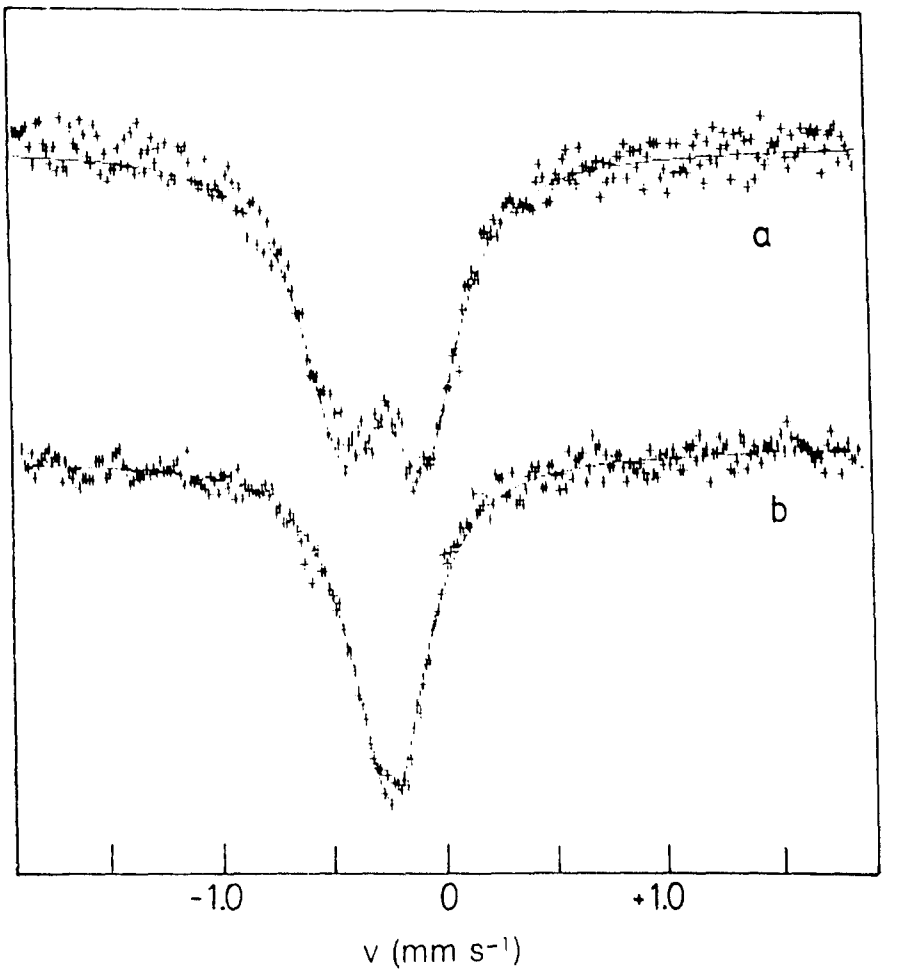
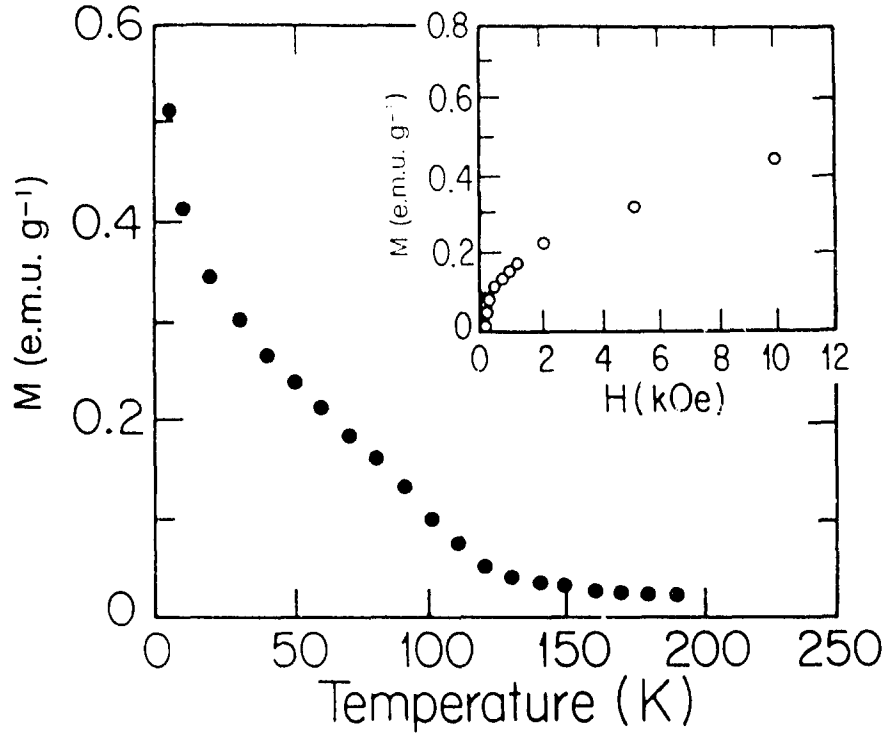


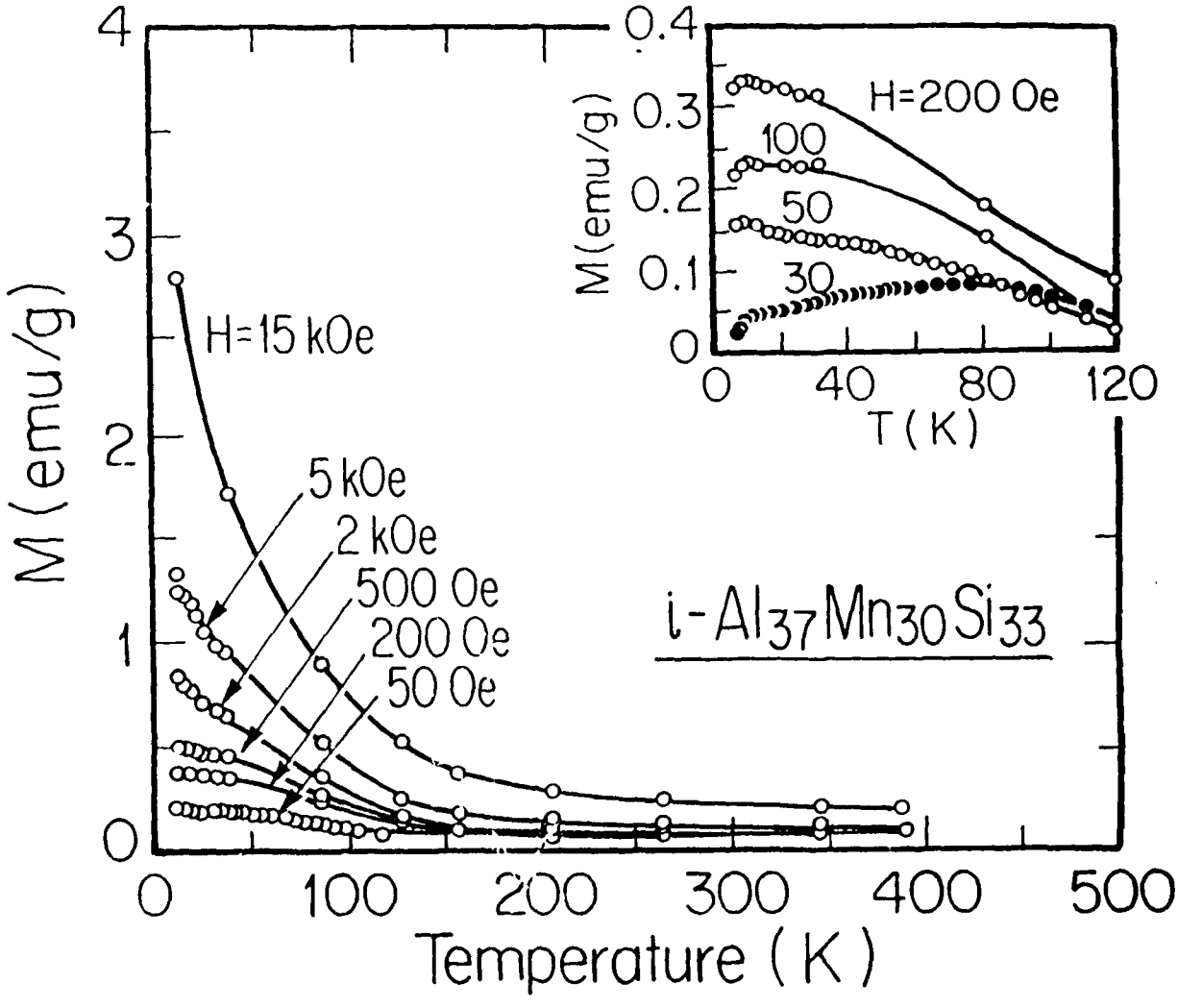
Comparison of Mössbauer spectra for (*a*) crystalline $Ti_2Ni_{0.85}Fe_{0.15}$ and (*b*) QC $Ti_{56}Ni_{23}Fe_5Si_{16}$ (Dunlap *et al.* 1989a).

Fig. 1



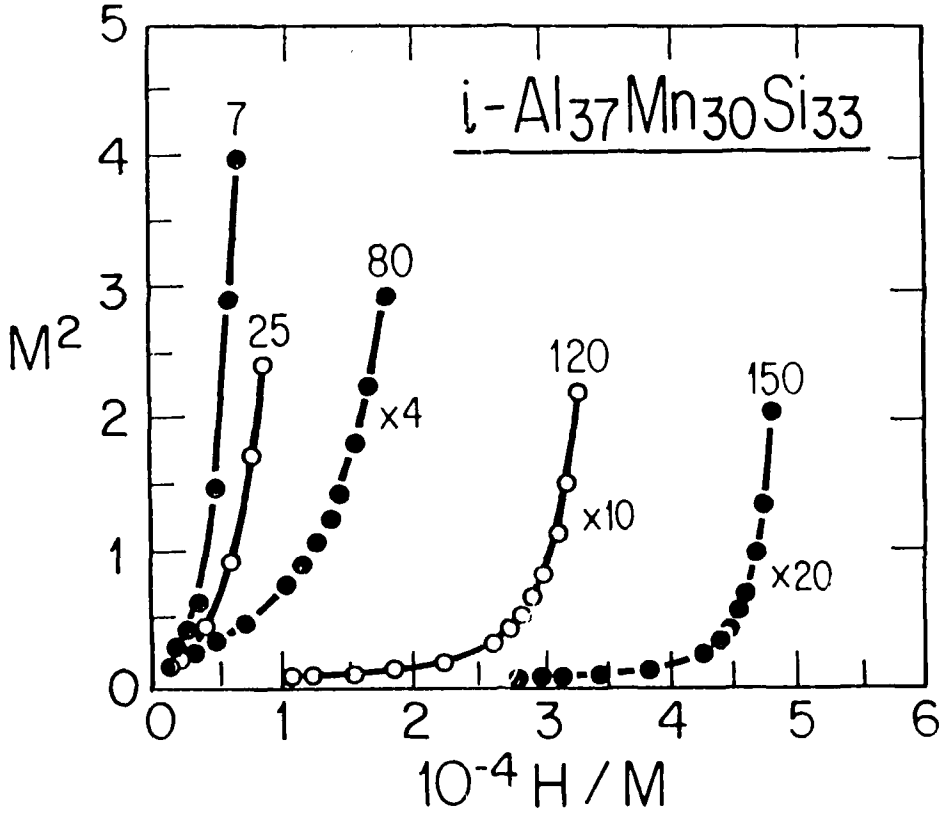
Temperature dependence of magnetization at $H = 1\,T$ in $Al_{55}Mn_{20}Si_{25}$ QC (Dunlap *et al.* 1989b). The inset shows the field dependence of magnetization for the same QC at $T = 10\,K$.

Fig. 2



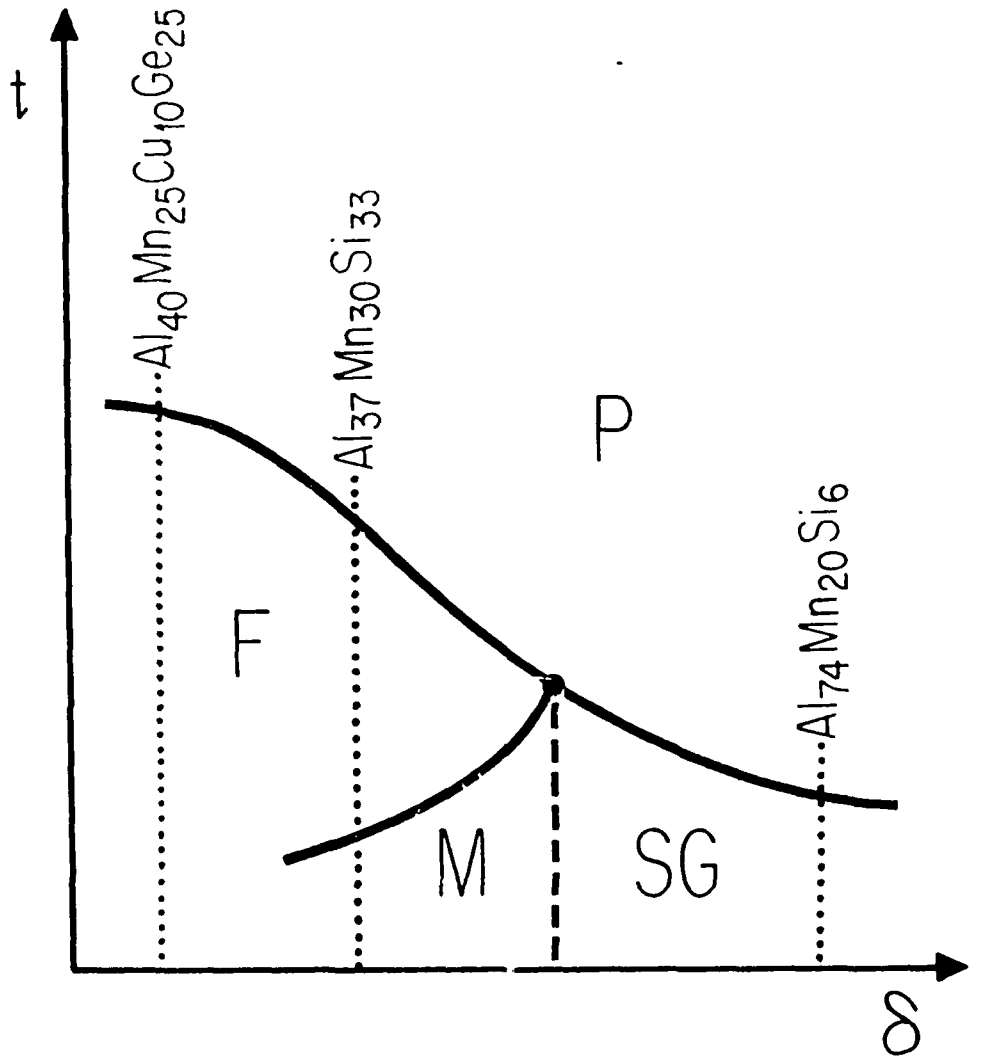
Temperature dependence of magnetization of icosahedral $Al_{37}Mn_{30}Si_{33}$ measured in various applied fields (Chatterjee et al. 1990)

Fig. 3



Arrott plot of field and temperature dependent magnetization for $Al_{37}Mn_{30}Si_{33}$ QC's (Chatterjee et al. 1990)

Fig. 4



Sellmyer-Nafis (1985) phase diagram for random exchange system. $t = k_BT/J_o$, $\delta = \Delta J/J_o$, F = ferromagnetic, P = Paramagnetic, S.G. = Spin-glass and M = mixed magnetic phase fields. Some of the QC's reviewed herein are located on the δ axis.