Distribution of magnetic-moment magnitudes in an Al-Mn-Si quasicrystal

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Magnetic-susceptibility measurements on quasicrystalline i-$Al_{74}Mn_{20-x}V_xSi_6$ establish that vanadium substitutes for manganese only at magnetic sites, and in a manner which preferentially occupies first those manganese sites with the largest local magnetic moments. Since vanadium possesses no local moment in this context, these measurements not only settle unequivocally the question concerning the relative proportion of magnetic and nonmagnetic manganese atoms in i-$Al_{74}Mn_{20}Si_6$, but also enable the actual distribution function of magnetic-moment magnitudes to be determined.

It is now definitely established[1,2] that two separate classes of Mn sites exist in icosahedral (or i-phase) Al-Mn-Si quasicrystals, distinguished by the possession or absence of a localized magnetic moment. However, beyond this fundamental assertion, answers to other more detailed questions, such as (a) what fraction of the Mn sites possess a local moment, (b) what is the distribution of magnetic moment magnitudes on the "magnetic" sites, and (c) what are the structural implications, remain either completely unknown (b) or are speculative [(a) and (c)] at the present time. Indeed, several groups of workers whose measurements also indirectly support the notion of two such classes of Mn sites, offer widely differing opinions as to the fraction of sites in the two classes.[3–6] It is the purpose of the present paper to answer questions (a) and (b), which is achieved by obtaining the first recorded preferential substitution of the magnetic sites in a quasicrystal, and to discuss the relevance of these findings to (c).

In Ref. 1 a combination of Mössbauer and magnetic-susceptibility measurements on iron-doped i-$Al_{74}Mn_{20}Si_6$ was used to establish firmly that *at least* 7.5/20 (or about 37%) of the Mn sites are nonmagnetic in this quasicrystal (in the sense of not possessing a local magnetic moment on the time scale of the experiments). In addition, since the sample exhibits magnetism in the bulk via a Curie-Weiss susceptibility, one could also infer that a significant fraction (and *at most* 63%) of the Mn sites must be magnetic in this same sense. It was speculated, via a structural model[1] involving interconnected Mackay icosahedra,[7] that a ratio of about 40% to 60% nonmagnetic to magnetic sites could be rationalized in terms of an icosahedral connectivity close to that expected for Penrose tile packings[8–10] but no conclusive evidence was available.

The appearance (or otherwise) of a magnetic moment on a 3d transition-metal (TM) atom when doped into a metal (M) is determined by a balance between intra-TM Coulomb forces and a coupling, via V_{sd} matrix elements, to penetrating host conduction electrons.[11] For a fixed M, local-moment formation is known[11,12] to peak near the center of the 3d series (Cr,Mn) and to decrease progressively along the series (V,Fe), (Ti,Co), (Sc,Ni). For M = Al the tendency towards local-moment formation is weak, and only Cr and Mn are known experimentally to retain local moments in some circumstances.

It is evident from earlier work that Mn in i-(Al-Mn-Si) is so close to the moment formation borderline that the retention (or not) of a Mn moment is actually a function of the distribution of Al nearest neighbors (NN). For a situation of this kind[11] the term which dominantly decides the question of moment formation is $|V_{sd}|^2$, with small values of $|V_{sd}|^2$ favoring moment formation. If, as seems highly likely, $|V_{sd}|^2$ decreases as a function of sd overlap (or nearest-neighbor Mn-Al distance) then it is the Mn in the larger Al "cages" of the quasicrystalline environment which are magnetic. Since there is a monotonic decrease in TM atom size from Sc to Ni *in equivalent environments* (as measured by the lattice dimensions of fcc, hcp, and bcc pure TM metal structures, where they exist[13]) we might expect Fe, Co, or Ni dopants in i-Al-Mn-Si to replace Mn (if at all) at dominantly nonmagnetic sites and Sc, Ti, or V to prefer magnetic sites. If so, the latter atoms substituting *without moment* for *magnetic* Mn atoms, would be able to probe directly the distribution of Mn magnetic moments in the quasicrystal.

In this article we confirm the general validity of this simple picture by preparing samples of, and carrying out magnetic susceptibility measurements on i-$Al_{74}Mn_{20-x}V_xSi_6$ ($x=0,2,4,6,8,12$). Alloys of $Al_{74}Mn_{20-x}V_x$ ($0\le x\le 12$) ingots were prepared by induction melting of high-purity Al, Mn, V, and Si in a pyrolytic boron-nitride crucible under argon atmosphere. Ribbon samples of about 1 mm width and 30 μm thickness were obtained by melt-spun technique on a copper wheel $\approx$20 cm in diameter rotating at 2000 revolutions/min (rpm). The solidification process was conducted in an enclosure filled with argon. X-ray diffraction measurements confirm the icosahedral symmetry in all the alloys with a trace of fcc Al. The Al content up to $x=5$ is constant at about 1% but above $x=5$ increases slightly with V concentration. Powder x-ray diffraction patterns as a function of V content are shown in Fig. 1. Here the indexing scheme of Elser[14] was used. We calculate the lattice parameters a_R [e.g., $=(19.311/2\pi)d_{322\,101}$]. The a_R value increases linearly from 4.595 to 4.660 Å as V increases from 0 to 12. This

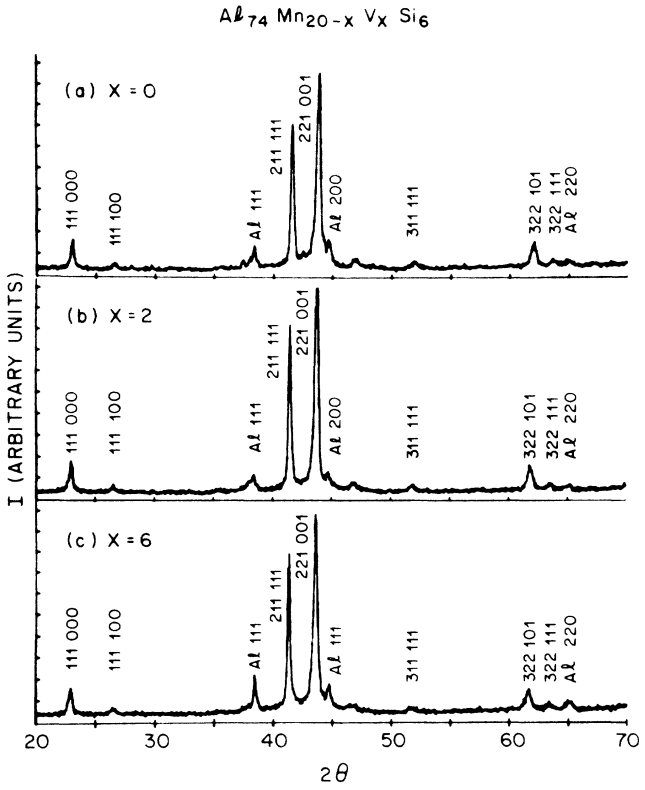

FIG. 1. X-ray diffraction patterns of melt-spun $Al_{74}Mn_{20-x}Fe_xSi_6$ for $x=0$, 2, and 6.

is in contrast with the $Al_{74}Mn_{20-x}Fe_xSi_6$ $(0\leq x\leq 7.5)$ system where a_R decreases with Fe concentration from 4.595 to 4.571 Å. This is consistent with the difference in atomic size of the elements in comparable (i.e., quasi-close-packed) environments. The magnetic susceptibility was measured by the Faraday method from 4.2 to 300 K.

In Fig. 2 we show the magnetic susceptibility χ as a function of temperature T for the six different V concentrations x. The data have been quantitatively fitted, between 20 and 150 K,[15] to a Curie-Weiss form

$$\chi=\{N_0C(x)/[3k(T+\Theta)M]\}+\chi_0 \text{ emu/g} \quad (1)$$

in which N_0 is Avogadro's number, $C(x)$ the Curie amplitude, k Boltzmann's constant, Θ the Weiss temperature, M the molecular weight per formula unit, and χ_0 a temperature-independent Pauli term, with values as set out in Table I. The mean magnetic moment $\bar{\mu}(x)$ per TM site is seen (Table I) to decrease monotonically with increasing V concentration x and to reach very small values for large x, confirming the expectation that V enters with zero (or close to zero) local moment.

Assuming the existence of an (at least approximate) one-to-one mapping of x and magnetic moment per Mn $\mu(x)$, such that in the increment $x\rightarrow x+dx$ the incremental V atoms replace Mn of moment $\mu(x)$, we can therefore express

$$C(x)=\int_x^{20}\mu^2(y)dy\ . \quad (2)$$

In Fig. 3(a) we now plot $C(x)$ versus x, joining smoothly the $C(x)$ data of Table I. Using this curve we now plot [Fig. 3(b)] the square root of its negative first derivative which, from Eq. (2), is

$$[-dC(x)/dx]^{1/2}=\mu(x) \quad (3)$$

and provides a direct experimental measure of the x dependence of magnetic moment per Mn.

Clearly, from Fig. 3(b), the first V doped into i-$Al_{74}Mn_{20}Al_6$ (i.e., $x\approx 0$) replaces Mn with a moment of about $2.2\mu_B$.[16] Additional V substitutes for Mn with smaller moments until finally, as V concentration approaches a value near to the i-phase stability limit ($x\approx 12$), it replaces Mn with very small (and possibly even zero) moment. Also, from this same figure, it is apparent *at least* $\approx\frac{12}{20}$ (or 60%) of the i-phase Mn sites possess a nonzero local magnetic moment. Since we established earlier[1] that Fe replaces Mn in wholly *nonmagnetic* Mn sites to a concentration $\approx\frac{7.5}{20}$ (or 38%), it follows conclusively that the ratio of magnetic to nonmagnetic Mn in i-$Al_{74}Mn_{20}Si_6$ is close to 60:40 in agreement with

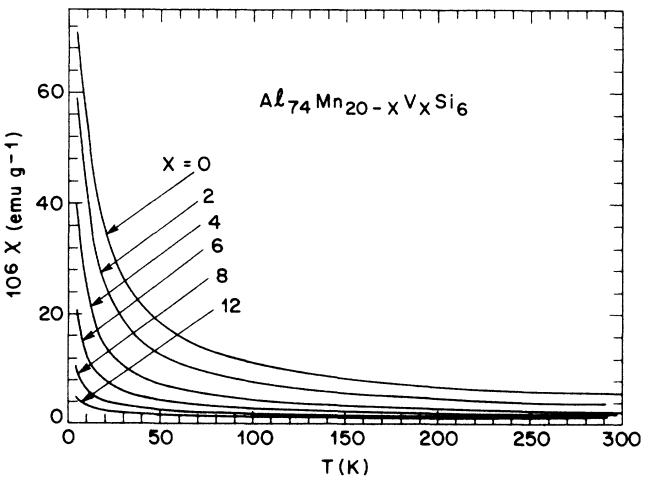

FIG. 2. Temperature dependence of the magnetic susceptibility of quasicrystalline i-$Al_{74}Mn_{20-x}V_xSi_6$ for six different concentrations between $x=0$ and $x=12$.

TABLE I. The Curie amplitude $C(x)$, Weiss temperature Θ, and Pauli paramagnetic component χ_0 as deduced from measured magnetic susceptibility for quasicrystalline samples i-$Al_{74}Mn_{20-x}V_xSi_6$ by fitting to Eq. (1) for temperatures between 20 and 150 K. Also shown is the molecular weight M per formula unit and the mean magnetic moment $\bar{\mu}(x)$ per total TM site.

x	$C(x)/\mu_B^2$	Θ (K)	χ_0 (10^6 emu/g)	M (g)	$\bar{\mu}(x)/\mu_B$
0	25.6	9	2.4	3264	1.13
2	16.6	7	1.7	3256	0.91
4	9.1	5	1.2	3248	0.67
6	4.5	6	1.2	3240	0.47
8	2.1	6	1.1	3232	0.32
12	0.9	3	1.0	3216	0.21

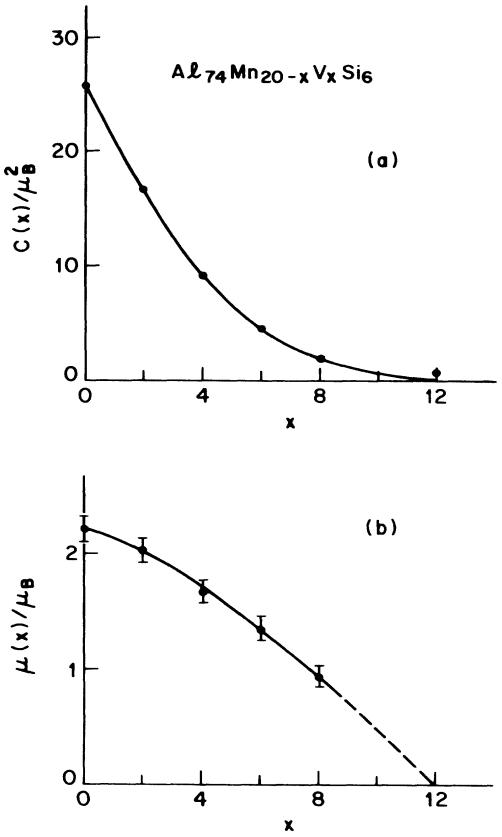

FIG. 3. (a) Concentration dependence of the Curie amplitude $C(x)$ of Eq. (1). The closed circles are direct experimental values from Table I, and the curve is a smooth interpolation between them (see text for a discussion of the data point at $x=12$). (b) The magnetic-moment magnitude $\mu(x)$ per Mn as derived from (a) by use of Eq. (3).

the assumption of Ref. 1. The very different estimates of Refs. 5 and 6, which are obtained via high-field magnetic-moment measurements down to low temperatures, appear to result from the difficulties associated with a quantitative description of the distribution of local-field magnitudes in actual or incipient spin glasses.[17]

The findings represented by Fig. 3(b) conform with a picture of V substituting most readily (i.e., first) for those Mn in the largest Al cages, and thereafter at progressively smaller sites. In terms of the i-phase model of Ref. 1, V can eventually substitute for essentially all Mn sites adjacent to broken MI "bonds," but not for those (more compact) sites adjacent to nonbroken bonds. It therefore acts as a complement to Fe which, within the model,[1] can substitute only for Mn at the (nonmagnetic) nonbroken bond sites. A recent EXAFS study of i-$Al_{74}Mn_{20-x}V_xSi_6$ does indeed indicate that V substitutes for Mn with larger than average Mn-Al NN distance.[18]

The existence of a small mean magnetic moment $\bar{\mu}=0.21\mu_B$ at $x=12$ (Table I) is, at first site, in conflict with the extrapolation of $\mu(x)$ to zero at $x=12$ in Fig. 3(b). It could indicate the retention of a small moment on V throughout (although we consider this to be extremely unlikely). More likely it is a confirmation either of the breakdown of the i-phase structure near this stability limit[19] or of the one-to-one mapping assumption of x and $\mu(x)$. With regard to the latter, it may be that when $x \rightarrow x+dx$, the incremental V atoms may not replace Mn which all possess precisely the same value $\mu(x)$ of magnetic moment. They may sample a range of moments about $\mu(x)$, an effect which will become most apparent when $\mu(x) \rightarrow 0$ and give rise to a spurious moment in this limit. One final possibility is that the quasicrystalline composition (in the light of the observed presence of a trace of fcc Al), may slightly exceed the designated Mn_{20-x} in Mn content.

Finally, combining Fig. 3(b) with the knowledge acquired from Ref. 1 that $\mu(x)$ is zero for those x values $12<x<20$ not physically realizable by V substitution, we can now plot the distribution $p(\mu)$ of magnetic-moment magnitudes μ for the complete set of Mn sites in i-$Al_{74}Mn_{20}Si_6$. It is shown in Fig. 4, where it has been normalized to $\int p(\mu)d\mu=1$, with 40% of this area being under the $\mu=0$ δ function. The mean value $\bar{\mu}$ over all Mn sites is about $1.1\mu_B$, while the mean value over magnetic sites only is closer to $1.5\mu_B$.

It remains finally to discuss the question of whether Fig. 4 is indeed relevant for the V-free system or whether some of the reduction in $\mu(x)$ with increasing x (Fig. 3) is produced by the V itself, via a filling of minority spin holes at remaining Mn neighbor sites. Existing evidence[20] suggests that such an itinerant effect for V is significantly nonzero only out to distances ≈ 3 Å. Since the V-Mn distances of relevance in the quasicrystal are

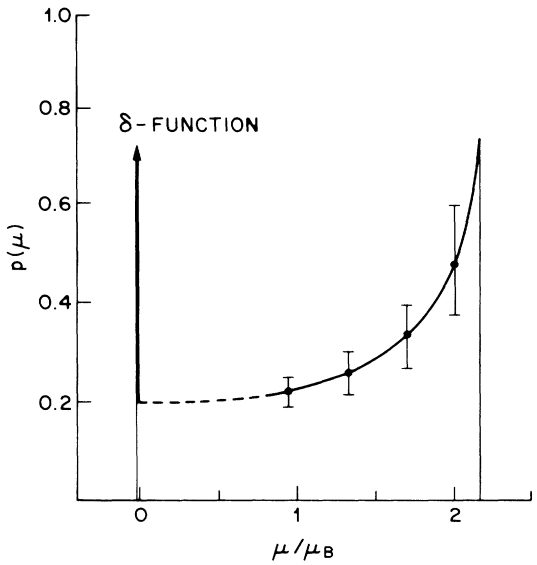

FIG. 4. The distribution function $p(\mu)$ of Mn atomic magnetic-moment amplitudes in i-$Al_{74}Mn_{20}Si_6$, as deduced graphically from Fig. 3(b) incorporating the additional knowledge that 40% of the Mn [formally those sites corresponding to $12<x<20$ in Fig. 3(b)] are nonmagnetic. The distribution $p(\mu)$ is normalized to unity, with 40% of the area being under the δ-function peak at $\mu=0$.

$\gtrsim 4.5$ Å we consider such an effect to be unlikely in the present context, and consequently that Fig. 4 does adequately portray the distribution of Mn magnetic moments in i-$Al_{74}Mn_{20}Si_6$.

In summary, we have successfully obtained a preferential substitution of the *magnetic* sites in i-$Al_{74}Mn_{20}Si_6$ in a manner which enables us to deduce, for the first time, the distribution function of magnetic-moment magnitudes in a quasicrystal. We find that close to 60% of the Mn possess nonzero magnetic moments, with magnitudes which extend from arbitrarily small values to a maximum of $2.2\mu_B$. The results are generally supportive of the model of quasicrystalline structure presented in Ref. 1.

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