Local-moment enhancement in an Al₇₄Mn₂₀Si₆ quasicrystal induced by nonmagnetic-iron doping

M. Eibschütz, M. E. Lines, H. S. Chen, J. V. Waszczak, G. P. Espinosa, and A. S. Cooper AT&T Bell Laboratories, Murray Hill, New Jersey 07974 (Received 5 June 1989)

In quasicrystalline (icosahedral-phase) $i-Al_{74}Mn_{20}Si_6$, about 60% of the Mn are known to possess local magnetic moments (on a time scale sufficient for them to contribute a Curie-Weiss term to magnetic susceptibility) and 40% not. In $i-Al_{74}Mn_{20-x}Fe_xSi_6$, iron enters without a local moment and preferentially substitutes for "nonmagnetic" Mn. We report a careful measurement and analysis of magnetic susceptibility for the iron-doped *i* phase between x = 0 and 5 and establish that magnetic response is not completely independent of x. For very small x, iron *increases* the mean magnetic moment per transition metal. A tentative explanation is given in terms of the "brokenbond" α -phase model of the quasicrystal.

It is now clearly established¹⁻³ that icosahedral (*i*-phase) Al-Mn-Si quasicrystals possess two separate classes of Mn sites distinguished by the presence or absence of a localized magnetic moment on the time scale ($\approx 10^{-13}$ s) of thermal relaxation. With this definition of "localized moment" the two site classes manifest their difference by their respective contribution, or lack of contribution, to a Curie-Weiss term in magnetic response. In particular, for *i*-Al₇₄Mn₂₀Si₆ (a composition close to the optimum for completeness of *i*-phase formation) the ratio of magnetic to nonmagnetic sites is known to be close to $\frac{12}{8}$.

Questions concerning the retention or loss of local *d*electron magnetic moments when 3*d* transition metals are inserted into a metallic matrix were a topic of intense and fruitful research activity in the 1960's and 1970's.⁴⁻⁸ Theoretically, the problem concerns a competition between Coulomb and Hund's-rule exchange forces on the one hand (which favor local-moment formation) and the coupling V_{sd} between transition metal *d* electrons and the *sp* electrons of the host metal (which encourages itinerancy and hence destabilizes local moments). The former interactions are largest near the center of the transitionmetal series (i.e., Mn), while the latter increase with the valency of the metal (e.g., along the series Cu,Zn,Al).

In fcc Al metal itself, V_{sd} is large enough to destabilize local magnetic moments on the magnetic susceptibility time scale for all 3d transition-metal solute atoms, i.e., they remain Pauli paramagnets. However, in the case of Mn (for which moment formation forces are largest), the balance is almost critically close to moment formation⁹ and, indeed, moments have been detected by x-ray induced photoemission spectroscopy¹⁰ on a time scale $\approx 10^{-15}$ s. It therefore comes as no surprise to find that Al-Mn and Al-Mn-Si alloys in the Al-rich *i*-phase compositional regime also manifest spin-fluctuation phenomena related to borderline magnetic-moment formation. More intriguing is the notion that this implied ultrasensitivity of magnetic properties to small perturbations of environment can perhaps be utilized to probe the local structure of the i phase itself, or at least to test the viability of models that purport to represent it.

The fundamental building block of the icosahedral Al-Mn phase is^{11,12} the $Al_{42}Mn_{12}$ Mackay icosahedron¹³ (MI) found in the crystalline ternary alloy¹⁴ α -Al₁₀₀Mn₂₄Si₁₄. In Al-Mn-Si alloys, no realistic effort has yet been made to distinguish between the roles of Al and Si so that, in the context of these ternaries, Al refers to a generic "Al/Si atom" without additional elaboration. The 12 Mn atoms of the MI occupy the 12 icosahedral vertices. Each is surrounded by six intra-MI Al nearest neighbors (NN's) and, in the α phase, by either four or five additional inter-MI "glue" Al NN's.¹⁴ In the α phase these glue atoms connect the MI along all eight (111) directions of the bcc lattice upon which the MI are centered. In the *i* phase the MI maintain their orientational integrity, but their connectivity via the glue atoms is modified. In particular, for *i* phase composition Al₇₄Mn₂₀Si₆ the number of glue atoms per MI is significantly reduced from that of the α -phase crystal. The implied reduction in connectivity appears to be accomplished by the "breaking" of some inter-MI "bonds" (in some sense) while retaining the essential α -phase form of the others.^{3,15}

Since the crystalline α phase is a Pauli paramagnet (see Fig. 1), the Mn atoms adjacent to "unbroken" bonds in the *i* phase are presumed to be nonmagnetic (in the Curie-Weiss sense), a supposition supported by doping with nonmagnetic iron^{1,2} (which selectively substitutes only for nonmagnetic Mn) and with nonmagnetic vanadium³ (which selectively substitutes only for magnetic Mn). Since Fe is smaller than Mn in an equivalent environment, and V is larger, the findings suggest a model in which Fe substitutes for Mn at the smaller Mn sites (adjacent to unbroken MI bonds), while V prefers the larger Mn sites (adjacent to broken MI bonds). Since the latter have the smaller *sd* overlap, and smaller V_{sd} encourages local moment formation, a self-consistent model^{1,3} for *i*

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FIG. 1. Temperature dependence of the magnetic susceptibility of quasicrystalline *i*-Al₇₄Mn_{20-x}Fe_xSi₆ for x=0,2,4 and of the crystalline material α -Al₁₀₀Mn₂₄Si₁₄.

phase Al-Mn-Si locates nonmagnetic Mn adjacent to unbroken (α -phase-like) MI "bonds" and magnetic Mn adjacent to broken MI "bonds." Within this model we do not wish to imply the existence of two approximately well-defined crystallographic Mn sites, but rather two distributions (or classes) of Mn sites that together span a whole range of Al-"cage" local environments,¹⁶ as elaborated in the following.

The only apparent experimental conflict with this picture (of which we are aware) arises from the x-rayabsorption fine structure (XAFS) work of Ma and Stern, ¹⁷ who conclude that the mean local environments of Mn and Fe in *i*-Al₇₄Mn_{17.6}Fe_{2.4}Si₆ are the same within experimental error. Their suggestion is¹⁵ that small amounts of Fe may substitute approximately randomly (i.e., into both magnetic and nonmagnetic Mn sites) at small concentrations. For larger concentrations there is already neutron-diffraction support (cited in Ref. 15) for the picture of preferential Fe substitution.

It was to clear up this point that the work reported here was initiated. Specifically we have repeated more carefully, and for more iron concentrations, the susceptibility measurements on $i-Al_{76}Mn_{20-x}Fe_xSi_6$ first reported in Table I of Ref. 1. If nonmagnetic Fe is substituting partly for magnetic Mn at low iron concentrations (i.e., small x) then the numerator of the Curie-Weiss component of magnetic susceptibility should initially decrease as a function of x from its value in $i-Al_{76}Mn_{20}Si_6$. Somewhat to our initial surprise, this numerator (which is proportional to the mean paramagnetic moment per transition-metal atom) was observed to increase rather abruptly for small x, settling down to a more constant value at larger x. A model of nonmagnetic Fe substituting preferentially for nonmagnetic Mn would, in the absence of interaction effects, dictate a completely xindependent Curie-Weiss amplitude. The explanation therefore must involve the manner in which the dopant Fe perturbs its structurally very sensitive Mn neighbors. This explanation, as we shall see following, not only supports the details of the random connectivity model set out in Ref. 3 but also suggests the likely reason for the XAFS finding of Ref. 17.

Alloys of $Al_{74}Mn_{20-x}Fe_xSi_6$ ($0 \le x \le 5$) were prepared by induction melting of high-purity Al, Si, Mn, and Fe in a boron nitride crucible under argon atmosphere. Ribbon samples of about 1-mm width and 30- μ m thickness were obtained by melt spin 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. The magnetic susceptibility was measured by the Faraday method from 4.2 to 300 K. In Fig. 1 we show the magnetic susceptibility χ as a function of temperature for three different Fe concentrations, x=0,2,4, and for the crystalline α phase. The *i*phase curves for x = 1,3 fall, respectively, between those for x=0,2 and x=2,4, while that for x=5 is barely distinguishable from x=4 on the scale of Fig. 1.

The experimental susceptibility data have been analyzed between 20 and 150 K by least-squares fitting to a Curie-Weiss form,

$$\chi = C / (T + \Theta) + \chi_0 \quad (\text{emu/g}) , \qquad (1)$$

with the results set out in Table I. The restriction of 20 K as a lower bound for application of Eq. (1) is necessitated by incipient spin-glass behavior that sets in at lower temperatures.¹ The upper bound of 150 K is chosen to limit any spurious perturbations of C produced by a possible temperature-dependent Pauli term χ_0 and particularly because of the known Kondo nature⁸ of Al(Mn) systems at elevated temperatures. We note that, whereas the Weiss temperature Θ is essentially independent of x, both the Curie amplitude C(x) and the "Pauli" term $\chi_0(x)$ exhibit interesting concentration dependences that lie outside the 70% (i.e., one standard deviation) confidence limits.

In this paper our primary interest will center upon

TABLE I. The Curie amplitude C, Weiss temperature Θ , and Pauli paramagnetic component χ_0 as deduced from measured susceptibility for quasicrystalline $i\text{-Al}_{74}\text{Mn}_{20-x}\text{Fe}_x\text{Si}_6$ $(0 \le x \le 5)$ by least-squares fitting to Eq. (1) for temperatures between 20 and 150 K. Also shown is the derived value of mean magnetic moment $\overline{\mu}/\mu_B$ per *total* transition-metal site and (bottom line) the one standard deviation (i.e., $\approx 70\%$ confidence) limits of the fits.

	С	Θ	<i>X</i> 0	
<u>x</u>	$(10^{-6} \text{ emu K/g})$	(K)	(10^{-6} emu/g)	$\overline{\mu}/\mu_B$
0	932	9.3	2.2	1.10
0 ^a	893	9.0	2.4	1.08
1	1143	8.5	2.2	1.22
2	1034	8.3	2.1	1.16
3	1180	7.7	1.6	1.24
4	1234	10.3	0.9	1.27
5	1131	8.0	1.2	1.21
	(±110)	(±2.5)	(±0.6)	(±0.06)

^aA second, independently prepared sample.

C(x), see Fig. 2, which rises from a value of 900 ± 100 emuK/g at x=0 (double checked using two independently prepared samples) to about 1150 ± 100 for x > 3. In spite of the large error bars, the qualitative nature of the findings is persuasive. In order to seek its explanation we return first to Fig. 4 of Ref. 3, which plots the distribution function of magnetic moments in *i*-Al₇₄Mn₂₀Si₆ as measured by V substitution. We note that while some local Mn moments are relatively stable (with magnitudes in excess of $2\mu_B$ per Mn), and other Mn moments clearly possess no local moments at all, yet others are magnetic with small moments (certainly below $1\mu_B$ and possibly even arbitrarily close to zero). The latter must be critically close to the borderline between possessing and not possessing a local moment and therefore must be ultrasensitive to even the smallest perturbation of environment.

Using a local-MI model for the *i* phase in which MI bonds are broken in a random fashion³ we may now tentatively identify these ultrasensitive sites. Within the model the observed 8:12 ratio of nonmagnetic to magnetic Mn dictates an average of close to three broken MI bonds per MI.³ From Fig. 3 we readily verify that three bonds can be removed in only three topologically distinct fashions, which we label as "3 linked," "3 unlinked" and "2 linked, 1 unlinked" (with respective probabilities 3:1:3) using a nomenclature made obvious from the figure. Examining the individual Mn sites in all these configurations we identify 28 equally probable classes, distinguished by the number of adjacent broken "bonds" (i.e., MI $\langle 111 \rangle$ linkages) of the site itself coupled with the broken-bond character of its five intra-MI NN Mn sites (Table II). The latter are relevant, since some glue "Al"



FIG. 2. The Curie amplitude C deduced as a function of iron concentration x for a sequence of quasicrystals *i*-Al₇₄Mn_{20-x}Fe_xSi₆ by least-squares fitting the measured magnetic susceptibility between 20 and 150 K to Eq. (1). The error bars represent the one standard deviation (or 70% confidence) limits of the data.



FIG. 3. Each pair of figures shows the ten outside front and ten inside rear faces of an icosahedron viewed along the same three-fold axis, say the positive (111) axis. Of these 20 faces, eight (shaded) are $\langle 111 \rangle$ type and are all fully bridged to NN icosahedra in the crystalline α phase. In *a*, *b*, and *c*, we show the three topologically distinct way in which three such $\langle 111 \rangle$ "bonds" can be broken. With bold heavy lines outlining broken-bond $\langle 111 \rangle$ faces, they are referred to as (a) 3 linked, (b) 2 linked, 1 unlinked, and (c) 3 unlinked broken-bond configurations in an obvious nomenclature. Solid circles are "magnetic" Mn; open circles are "nonmagnetic" Mn.

contribute to the bridging of two NN inter-MI $\langle 111 \rangle$ linkages.

Of the 28 classes, ten involve Mn which are adjacent to wholly unbroken bonds and are deemed to be nonmagnetic (in the sense of this paper). Of the remaining classes, which all involve magnetic Mn, we designate groups as follows (see Table II): D sites, adjacent to two broken bonds; C, B, A sites, adjacent to one broken bond but with, respectively, 2, 1, and 0 double-broken-bond intra-MI NN Mn.

If we presume that the number of glue Al and/or their mean Mn-Al distance decreases in the sequence A, B, C, D(as seems likely from their definition), then we must also anticipate that V_{sd} decreases and (correspondingly) magnetic-moment magnitude increases along this same sequence. This being so, the ultrasensitive Mn sites are the A sites. Upon examining the nonmagnetic sites (n=0 in Table II) we find that only those from 3-2-linked, 1-unlinked broken-bond unlinked and configurations (five of ten in Table II) are, adjacent to Asites. Moreover (Table II), these are, in general, the nonmagnetic sites with the largest Al "cages" (i.e., adjacent to those intra-MI NN Mn sites with the largest number of broken bonds).

If we now postulate that Fe atoms enter first the largest nonmagnetic Mn sites, and subsequently the progressive-

TABLE II. The 28 different Mn environments that arise with equal probability from a Mackay icosahedron (MI) with three randomly broken bonds (i.e., $\langle 111 \rangle$ linkages to NN MI). Each Mn environment is labeled according to the broken linkage topology (see Fig. 3), the number n (=0,1,2) of broken bonds adjacent to that site, and the numbers (a,b,c), a+b+c=5, of NN Mn sites with (a) doubly broken, (b) singly broken, and (c) unbroken bonds. The n=0 sites are nonmagnetic; the n=1,2 sites are magnetic. The subcategory types A, B, C, D for magnetic sites are discussed in the text.

	3 linked		3 unlinked			2 linked 1 unlinked		
Туре	n	(<i>a</i> , <i>b</i> , <i>c</i>)	Туре	n	(a , b , c)	Туре	n	(<i>a</i> , <i>b</i> , <i>c</i>)
				Mag	netic			
D	2	(1,4,0)				D	2	(0,4,1)
D	2	(1,3,1)						
С	1	(2,2,1)	A	1	(0,5,0)	В	1	(1,3,1)
С	1	(2,1,2)	A	1	(0,4,1)	В	1	(1,3,1)
B	1	(1,2,2)	A	1	(0,3,2)	В	1	(1,2,2)
B	1	(1,2,2)				В	1	(1,3,3)
B	1	(1,1,3)				A	1	(0,4,1)
						A	1	(0,3,2)
						A	1	(0,2,3)
				Nonm	agnetic			
	0	(1,2,2)		0	(0,3,2)		0	(1,3,1)
	0	(0,3,2)					0	(0,4,1)
	0	(0,2,3)					0	(0,3,2)
	0	(0,2,3)					0	(0,3,2)
	0	(0,1,4)						

ly smaller nonmagnetic sites, the findings for C(x) in Fig. 2 receive immediate explanation. The first Fe then not only enters sites adjacent to the most magnetically sensitive Mn sites, but the perturbation that it produces (by contracting the Al cage around it, since Fe is smaller than Mn in the same environment, and consequently expanding the Al cage around the NN A sites) is at its largest. At larger iron concentrations the perturbation becomes weaker and the sites filled no longer have any A-type NN's. We therefore anticipate an increase in mean magnetic moment (via A-site moment enhancement) for small Fe concentration x, progressively decreasing in magnitude as x increases and finally becoming independent of x for $x \gtrsim 4$ (i.e., $\frac{5}{10}$ of the total nonmagnetic concentration).

Although this picture is somewhat ad hoc (and the full

statistical implications have not been pursued in restricting the entire argument to MI with three, and exactly three, broken bonds per MI) it does have other interesting features. Thus, the large number of classes of site in Table II helps to explain the quasicontinuous distribution of electric field gradients observed in Mössbauer studies¹⁶ (which probe the nonmagnetic Mn sites) and the continuous distribution of Mn moments at the magnetic sites deduced from V substitution.³ Also, the fact that low concentrations of Fe enter first at the largest nonmagnetic sites (whose radial distribution of Al may not be that much smaller than the overall mean), while larger concentrations go into the smallest Mn sites in the entire complex, may help to explain why preferential site substitution via a determination of mean NN Al environment is only readily achieved at high Fe concentration.^{15,17}

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