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Magnetic behavior of $(\mathrm{Al,Ge})_{65}\mathrm{CuMn}$ quaternary alloy quasicrystals

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We report the results of field and temperature dependent magnetization measurements on $(\mathrm{Al,Ge})_{65}\mathrm{CuMn}$ quasicrystalline samples with ~22 and 24 at. % Mn. The Ge content is also kept ~25 at. %. The data for these samples are then compared with the data taken on samples with low Ge content (~10 and 0 at. %). $\mathrm{Al_{40}Ge_{25}Cu_{10}Mn_{25}}$, a composition very close to one of the alloys studied here, is reported [Tsai *et al.*, Jpn. J. Appl. Phys., **27**, L2252 (1988)] in literature as a ferromagnetic, icosahedral QC with large T_C. The detailed magnetic studies described here prove that the magnetism observed in these quaternary alloys is highly disordered. The two important observations made in our studies are (i) observation of short-range ferromagnetism in samples with high Ge and high Mn content, up to very high fields ($H=5$ T) and (ii) oscillatory magnetization (or existence of multiple minima in the M-T curves) observed for the same samples for $H \geqslant 1$ kOe. *© 2004 American Institute of Physics.* [DOI: 10.1063/1.1757651]

I. INTRODUCTION

Most reported quasicrystals in literature are not strongly magnetic. However, there are some scattered works in literature[1–7] where results of the studies on "magnetic quasicrystals" have appeared. Restricting our discussions to Al-based quasicrystals, it has been shown[2,3] that the icosahedral Al-Mn alloys have enhanced susceptibility as compared to the orthorhombic $\mathrm{Al_6Mn}$ crystalline phase. Hauser *et al.*[2] have shown that the icosahedral Al-Mn alloys show the presence of a local moment that increases with the square of the Mn concentration. However, in contradiction to this report, in literature, there is also a mention of nuclear-magnetic-resonance studies[8] that indicate no tendency of stronger magnetism in quasicrystalline Al-Mn as compared to the crystalline state. It is interesting to note that alloys with higher Mn concentrations (≥25 at. %) with about 20 at. % Ge (or about 30 at. % Si) show magnetic order[4,5] with a low moment, relatively high T_c and a high coercivity. On the other hand, alloys with lower Mn content are paramagnetic and normally show a spin-glass-like behavior.[1] Chatterjee *et al.*[6] have shown that the apparent magnetic order seen in high Mn content quasicrystals could probably be explained by the concentrated spin-glass behavior observed in these quasicrystals. The random magnetism found in the particular composition $\mathrm{Al_3Mn_{30}Si_{33}}$ was explained in terms of competing positive and negative Mn-Mn exchange interactions disordered over the quasicrystal structure.

Although various scattered data on the Al (Mn/TM) (Ge/Si) alloy system are available in literature, no systematic study has been done so far on this system to better understand the varied electronic behavior of this quaternary system. In a recent structural investigation[9] of such a series, namely $(\mathrm{Al}_{1-x}\mathrm{Ge}_x)_{65}\mathrm{Cu}_{10+y}\mathrm{Mn}_{25-y}$ $(0 \leqslant x \leqslant 0.4, 0 \leqslant y \leqslant 10)$ we showed that most of these alloys (including $\mathrm{Al_{40}Ge_{25}Cu_{10}Mn_{25}}$, the reported[4] magnetic quasicrystal) contain both icosahedral and decagonal phases. Although in the higher Ge content samples the trace of decagonal phase could not be identified by x-ray diffraction, TEM data proves the presence of decagonal phase beyond any doubt.

We present here the magnetic data on $(\mathrm{Al,Ge})_{65}\mathrm{CuMn}$ samples with ~22 and 24 at. % Mn a full-stop. The Ge content is also kept at ~25 at. %. The data for these samples are then compared with the data taken on samples with low Ge content (~10 and 0 at. %).

II. EXPERIMENTAL PROCEDURE

We report the field and temperature dependent magnetization measurements on $\mathrm{Al_{40}Ge_{25}Cu_{11}Mn_{24}}$, $\mathrm{Al_{42}Ge_{23}Cu_{13}Mn_{22}}$, $\mathrm{Al_{55}Ge_{10}Cu_{17}Mn_{18}}$, and $\mathrm{Al_{65}Cu_{10}Mn_{25}}$. $\mathrm{Al_{40}Ge_{25}Cu_{10}Mn_{25}}$, a composition very close to the first alloy studied here, is reported[4] in literature as a ferromagnetic, icosahedral QC with large T_C.

For the magnetization measurements at different fields with varying temperatures, the samples were first cooled at zero-field condition down to the lowest temperatures and then the respective field was applied and subsequently the data (magnetization) was taken with increasing temperatures up to 300 K. These data are denoted as zero-field-cooled (zfc) data. After the sample reached 300 K, the sample was again cooled down to lowest temperature of 5 K, this time in field; and then the data were collected as the temperature was increased from 5 to 300 K. This is denoted as fc data. The magnetization loops were also measured, in order to compare our data with the literature data. The M-H loops were measured at 5, 20, and 250 K.

III. RESULTS AND ANALYSIS

Figure 1 shows the M-H data taken on $\mathrm{Al_{40}Ge_{25}Cu_{11}Mn_{24}}$ at 5 and 250 K. The data taken at 20 K are not shown here as they overlap exactly with the 5 K data. At 5 and 20 K the full loops were measured, whereas only the first quadrangle data is reported for 250 K. The loops are very similar to the ones shown in Ref. 4. The nonsaturating

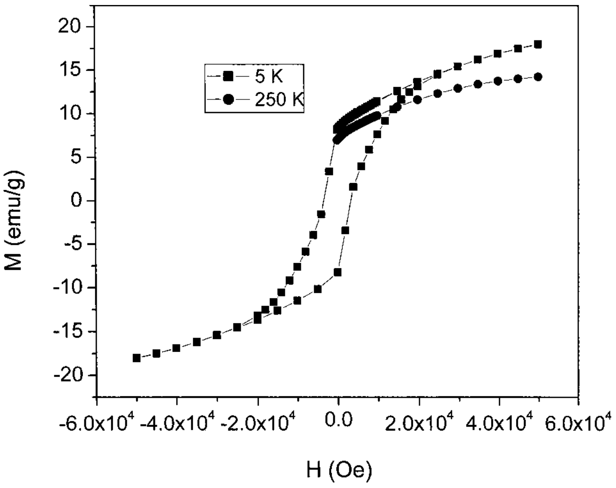

FIG. 1. M vs H plot for $Al_{40}Ge_{25}Cu_{11}Mn_{24}$ at 5 and 250 K.

M-H loops with narrow waist indicate the presence of disordered spin-glass-like transition in this system.

A. dc magnetization

Figure 2(a) shows the detailed M vs T plots taken for the $Al_{40}Ge_{25}Cu_{11}Mn_{24}$ at 1, 5, and 10 kOe. Figure 2(b) shows a detailed view of the low temperature data for 10 kOe, and 2(c) shows the M-T plots at very low fields of 30 and 50 Oe for the same composition. The fc data for 10 kOe is not shown in this figure for the sake of clarity.

Figure 3 shows the M-T plot of the same sample at very high field of 50 kOe (5 T). One of the key features of these M-T plots is the bifurcation in the zfc-fc data. Clearly, from Figs. 2 and 3, this bifurcation was noticed till the highest fields of 50 kOe. If T_f represents the temperature where zfc-fc curves meet, then we can say that T_f decreases with increasing fields. In the low field plots, T_f was not visible up to 300 K; disorder seems to persist even in the high-temperature and high-field limits of this quasicrystalline system. The zfc M-T data for all the other samples (except for this sample) are shown in Fig. 4.

For the sake of comparison all the plots in Fig. 4 are made for data at 1 kOe. Figures 5(a) shows a comparative plot of all these samples at low field values of 30/50 Oe and 5(b) shows the comparison of M-T data at 30 Oe for $Al_{42}Ge_{23}Cu_{13}Mn_{22}$ and $Al_{40}Ge_{25}Cu_{11}Mn_{24}$. At lower temperatures (~20 K) a peak is clearly visible in all the samples. This peak indicates the presence of some spin-glass-like transition in all these samples. Variation of T_{peak} with increasing field values is very typical and is shown for the two samples with high Ge and Mn content, in Fig. 6. Surprisingly, the peak is clearly visible even at the highest fields of 50 kOe (see Fig. 3). This observation is in contradiction to generally observed T_{peak} signifying the spin-glass transition. Another interesting point to note is that the T_{peak} increases with increasing Ge content in the sample. The last point to be mentioned about the T_{peak} is that in the sample with 0 at. % Ge (of similar Mn content), we observe a double transition at $T<75$ K.

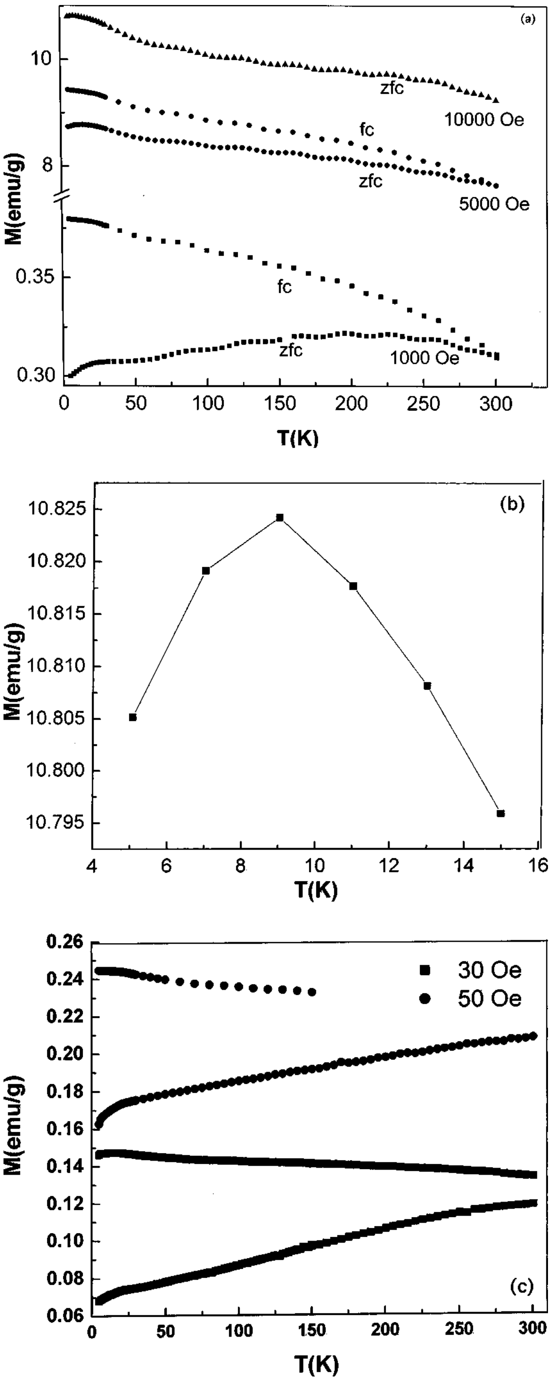

FIG. 2. (a) M vs T plot for $Al_{40}Ge_{25}Cu_{11}Mn_{24}$ at 1, 5, and 10 kOe. (b) shows a magnified view of the low temperature data for 10 kOe and (c) of this figure shows the M-T plots at very low fields of 30 and 50 Oe. ■ 1000 Oe, ● 5000 Oe, and ▲ 10 000 Oe.

At higher temperatures (see Fig. 1), the M-T plots are indicative of a ferro to para kind of transition present in the system. However, from these plots it is evident that the T_C for $Al_{40}Ge_{25}Cu_{11}Mn_{24}$ will be much beyond the room temperature of 300 K. In the absence of any better estimate, we have tried to interpret our magnetization data in terms of a theory based on itinerant electron model proposed by Wohlfrath and co-workers for very weak ferromagnets.[10] The estimated T_C for this sample turns out to be ~620 K, when the data was fitted to a form

$$\left[\frac{\sigma(0,T)}{\sigma(0,0)}\right]^2 = 1-2AT^2+A^2T^4, \quad \text{where } A=(1/2)T_C^{-2}.$$

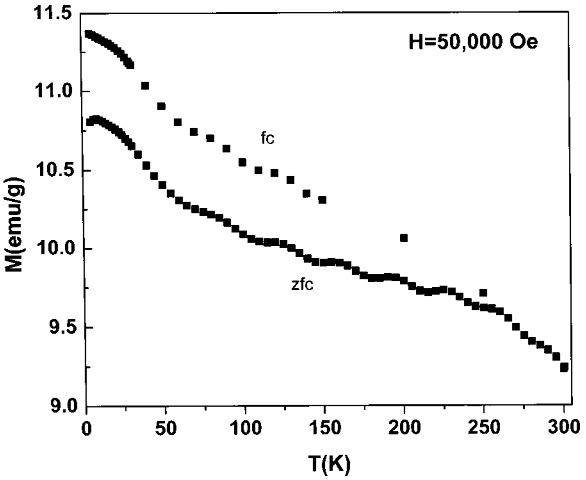

FIG. 3. M vs T plot for $Al_{40}Ge_{25}Cu_{11}Mn_{24}$ at 50 kOe.

The effective moments for all the samples were calculated from the high-field susceptibility data. A representative plot of high-field χ vs T and $1/\chi$ vs T (in this case at 1 kOe) from which these estimates were made, is shown in Fig. 7. The estimated effective moment values p_{eff} are given in Table I. Although the $Al_{40}Ge_{25}Cu_{11}Mn_{24}$ sample, with highest Mn content shows the highest effective moment, no real correlation of p_{eff} with the Mn content of the samples could be established.

B. ac magnetization

In order to define the spin-freezing temperature more accurately, the ac-susceptibility measurements (at 300 and 11 Hz) were also made. One set of such representative figures is shown in Fig. 8. A sharp peak was observed in the in-phase component χ', for both the frequencies. Although the plots almost overlap each other, when observed closely, the peak temperature for this sample shifts from 18.5 to 19 K as the frequency is changed from 11 to 300 Hz.

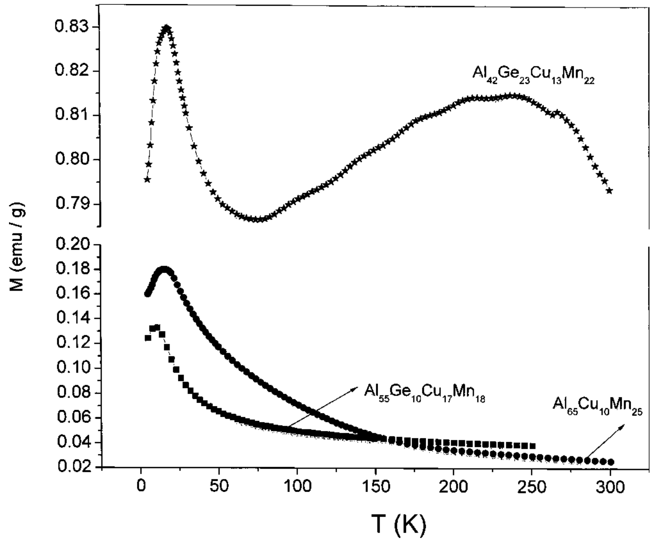

FIG. 4. The zfc M vs T plot for $Al_{55}Ge_{10}Cu_{17}Mn_{18}$, $Al_{65}Cu_{10}Mn_{25}$, and $Al_{42}Ge_{23}Cu_{13}Mn_{22}$ at 1 kOe magnetic field.

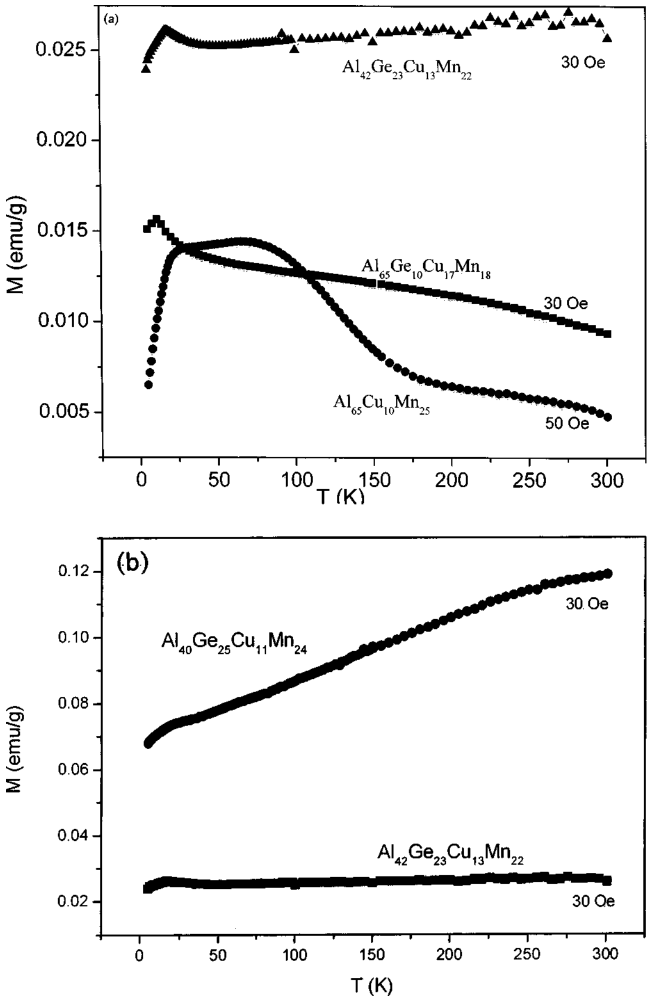

FIG. 5. (a) The zfc M vs T plot for $Al_{55}Ge_{10}Cu_{17}Mn_{18}$, $Al_{65}Cu_{10}Mn_{25}$, and $Al_{42}Ge_{23}Cu_{13}Mn_{22}$ at low magnetic field and (b) shows a comparison of the low-field plots for $Al_{42}Ge_{23}Cu_{13}Mn_{22}$ and $Al_{40}Ge_{25}Cu_{11}Mn_{24}$.

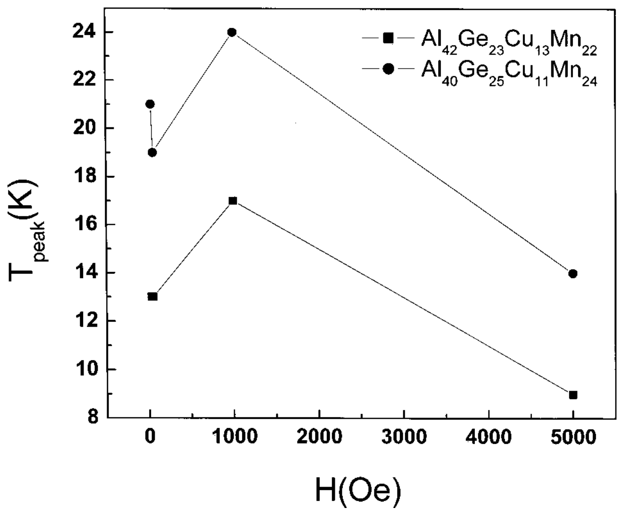

FIG. 6. The variation of T_{peak} values with field for $Al_{42}Ge_{23}Cu_{13}Mn_{22}$ and $Al_{40}Ge_{25}Cu_{11}Mn_{24}$.

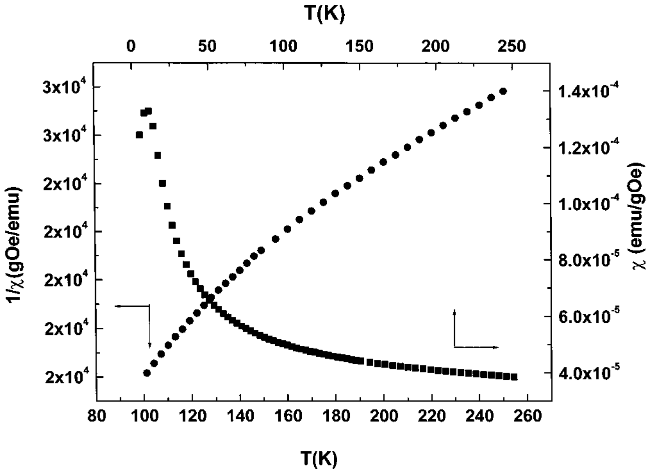

FIG. 7. χ vs T and $1/\chi$ vs T plot for $Al_{55}Ge_{10}Cu_{17}Mn_{18}$ at 1000 Oe.

The fractional relative change in $T_{\rm peak}[\Delta T_{\rm peak}/(T_{\rm peak}\Delta\log_{10}f)]$ for this change of frequency was found to be 0.018, a value comparable with other spin glasses reported in literature.[7]

C. Oscillations in *M-T* curves

The most unusual and striking feature that was observed only in samples with high Ge and high Mn content is the oscillatory magnetization that can be easily observed in the M-T curves shown in Figs. 2(a) and 4. These oscillations are very regular and start featuring at fields $H \geqslant 1$ kOe. Careful observation leads us to believe that these oscillations are not present at low-field values of 30 or 50 Oe. The origin of these oscillations is not clearly understood. A point to note in this regard is that the oscillatory behavior was observed only in samples with high Mn concentrations, in the M vs T plots. Keeping the trend, oscillations in samples with Mn (22 at. %) was less pronounced compared to the sample with Mn (24 at. %).

IV. DISCUSSION

For all the samples discussed here, the magnetization vs temperature data at low fields decrease with decreasing temperatures below ~20 K, indicating a spin-freezing at low temperatures in this system. Surprisingly, this feature is present in all the samples at higher fields (at least up to 1 kOe); and in some of the samples the trend is verified even at fields as high as 50 kOe (see Fig. 3). As is clear from Figs. 2 and 5, for samples with large Ge content ($Al_{42}Ge_{23}Cu_{13}Mn_{22}$ and $Al_{40}Ge_{25}Cu_{11}Mn_{24}$) the low-field M does not show a simple Curie-Weiss paramagnetism above the $T_{\rm peak}$. Instead, M shows a range over which ferromagneticlike behavior exists and as has been calculated for one of the samples, the T_c is estimated to be much higher than the room temperature, somewhere ~620 K. Even for fields $\geqslant 1$ kOe (see Figs. 1 and 4), non-Curie-Weiss-like behavior persists in these samples. This kind of M-T variation has been earlier observed[6] in Si rich quasicrystals that were described as concentrated spin glass with reentrant ferromagnetism. The bifurcation of zfc-fc plots with $T_f > T_{\rm peak}$ in these alloys support the idea of short-range ferromagnetism. The important point to note is that such bifurcation was observed even at very high fields ($H = 5$ T).

TABLE I. Estimated effective moment values ($p_{\rm eff}$).

Sample compositions	χ_o (emu/g Oe)	Effective moment ($p_{\rm eff}$)
$Al_{55}Ge_{10}Cu_{17}Mn_{18}$	3.83×10^{-5}	0.777
$Al_{65}Cu_{10}Mn_{25}$	2.47×10^{-5}	0.581
$Al_{42}Ge_{23}Cu_{13}Mn_{22}$	3.13×10^{-4}	0.641
$Al_{40}Ge_{25}Cu_{11}Mn_{24}$	9.16×10^{-4}	1.733

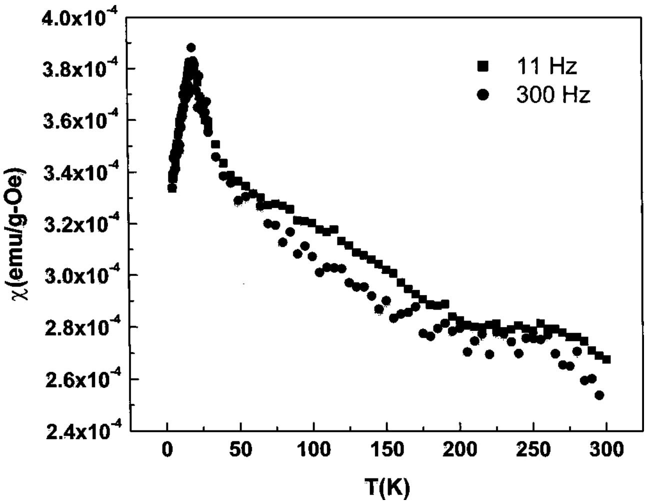

FIG. 8. ac χ data for $Al_{42}Ge_{23}Cu_{13}Mn_{22}$ taken at 300 and 11 Hz.

The low-field M-T data for low Ge content samples show a Curie-Weiss-like behavior above $T_{\rm peak}$. Presence of more than one magnetic phase is indicated in the low-field data for the sample with zero Ge content. For fields $\geqslant 1$ kOe (see Figs. 4 and 7) low Ge content samples show Curie paramagnetism with the estimated (from $1/\chi$ vs T plot) paramagnetic Curie temperature θ for $Al_{55}Ge_{10}Cu_{17}Mn_{18}$ as ~50 K (see Fig. 7) and θ ~13 K for $Al_{65}Cu_{10}Mn_{25}$.

The two main points in these results that need to be rationalized are (i) spin freezing in this quaternary quasicrystalline system at low temperatures (~20 K) and (ii) the oscillations (existence of multiple minima) in the M-T curves observed at high fields ($H \geqslant 1$ kOe) for samples with high Ge and high Mn content. The only atoms that can possess ferromagnetic moment in this quaternary system is Mn. The spin-glass behavior in a system arises due to the frustration of possible magnetic interactions. As suggested by Chatterjee *et al.*,[6] the spin-glass behavior with reentrant ferromagnetism present in high Si/Ge, high Mn content samples can be explained in the framework of Néel's theory of fine particles.[11] For this, one needs to consider the formation of ferromagnetic clusters that could interact positively or negatively, depending on the distances between the clusters. In the absence of any neutron-scattering data that gives the nearest neighbor Mn-Mn distances in icosahedral and decagonal (Al,Ge) CuMn quasicrystals (with high Ge, Mn content) or in the related compositions, explaining the formation of ferromagnetic/antiferromagnetic Mn-Mn interactions becomes very difficult. The only comment that can be clearly made is that between the two samples with high Ge and high Mn content, the magnetic moment significantly increases with the increase of Mn. As noted in the detailed microstructural studies made by the authors on these samples (see Ref. 9), in all the samples discussed here both icosahedral and decagonal phases were found[9] to be present throughout the series. It was found that the *I* phase stabilized with increasing Ge content and for the samples with high Ge along with high Mn concentrations, icosahedral grains were an order of magnitude larger (2.4 μm) in size as compared to decagonal grains (0.2 μm) (see Ref. 9).

It is thus possible that the samples with low Ge content that were found to have typical spin-glass behavior [Figs. 4 and 5(a)] with transition from spin glass to paramagnetic phase as reported in literature,[12] have evenly distributed ferromagnetic (*I*-phase) and nonmagnetic (*D*-phase) clusters, giving rise to classical spin-glass-like behavior. Whereas, owing to the growth[9] of *I* grains in samples with large Ge and large Mn content, the sizes of ferromagnetic clusters (where spins are strongly coupled within the cluster) increase. Thus in these samples we have large ferromagnetic clusters dispersed in a nonmagnetic matrix (*D* phase), creating strong disorder even at temperatures ~300 K, as T_C for samples with Ge [as compared to $Al_{37}Mn_{30}Si_{33}$ (Ref. 6)] increased to ~620 K.

As for the existence of multiple minima in M-T curves for the high Ge and high Mn content samples, we do not understand this phenomenon very well. Possibly these results suggest reentrant spin-glass behavior in the high Ge and high Mn content samples. However, it should be noted that the oscillations are observed at fields $\geqslant 1$ kOe and also at temperatures close to room temperature.

The presence of multiple phases in this system of alloys makes it very difficult to point out the origin of disorder. However, one conclusion that comes out clearly from this detailed investigation is that as we increase the concentration of icosahedral phase in the alloys, magnetic disorder increases.

An increase in magnetization and T_C has been indicated by Ido *et al.*[13] in crystalline $Mn_{1-x}M_xAlGe$ ($M = 3d$ metals) alloys when M is Cu. Whether such possibilities exist in quasicrystalline structure, giving rise to different magnetic phases, also need to be verified.

V. CONCLUSION

In conclusion one can say that the results of our detailed magnetic studies made on this quaternary alloy system finally proves that the magnetism observed in these quaternary alloys is highly disordered. As reported in literature,[9] all these alloys contain both icosahedral and decagonal phases. It is indicated that possibly the presence of multiple phases in this alloy system is the cause of such magnetic behavior. In order to better understand the origin of multiple minima in M-T curves as shown here, further experiments are required.

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[1] J. D. FitzGerald, R. L. Withers, A. M. Stewart, and A. Calka, Philos. Mag. B **58**, 15 (1988).
[2] J. J. Hauser, H. S. Chen, and J. V. Waszczak, Phys. Rev. B **33**, 3577 (1986).
[3] S. E. Youngquist, P. F. Miceli, D. G. Wiesler, H. Zabel, and H. Frazer, Phys. Rev. B **34**, 2960 (1986).
[4] A. P. Tsai, A. Inoue, T. Masumoto, and N. Kataoka, Jpn. J. Appl. Phys., Part 2 **27**, L2252 (1988).
[5] R. A. Dunlap, M. E. McHenry, V. Srinivas, D. Bahadur, and R. C. O'Handley, Phys. Rev. B **39**, 4808 (1989).
[6] R. Chatterjee, R. A. Dunlap, V. Srinivas, and R. C. O'Handley, Phys. Rev. B **42**, 233 (1990).
[7] I. R. Fisher, K. O. Cheon, A. F. Panchula, P. C. Canfield, M. Chernikov, H. R. Ott, and K. Dennis, Phys. Rev. B **59**, 308 (1999).
[8] W. Warren, H. S. Chen, J. J. Hauser, and R. C. O'Handley, Phys. Rev. B **32**, 7614 (1985).
[9] Ratnamala Chatterjee, Aloke Kanjilal, R. A. Dunlap, and O. N. Srivastava, Mater. Lett. **57**, 689 (2002).
[10] E. P. Wohlfrath, Phys. Lett. A **31**, 525 (1970).
[11] L. Neel, Ann. Geophys. (C.N.R.S.) **5**, 99 (1949).
[12] C. Janot, M. De. Boissieu, J. M. Dubois, and J. Pannetier, J. Phys.: Condens. Matter **1**, 1029 (1989).
[13] H. Ido, T. Kamimura, and K. Shirakawa, J. Appl. Phys. **55**, 2365 (1984).