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Mössbauer and Magnetic Investigation of the System $Mn_{5-x}Fe_xGe_3$ ($x = 0.5, 1.0$ and 1.5)*

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Mössbauer and magnetic measurements were carried out on the compositions $Mn_{4.5}Fe_{0.5}Ge_3$, Mn_4FeGe_3, and $Mn_{3.5}Fe_{1.5}Ge_3$. Data were obtained from liquid N_2 to about 600°K. The iron substitution takes place initially in the 4(*d*) sites of the $D8_8$ structure of Mn_5Ge_3 until one half of manganese is replaced; additional iron, then, may substitute in 6(*g*) sites. The postulated magnetic structure for Mn_5Ge_3 consists of ferromagnetic alignment of spins within the two sublattices and parallel alignment between them. When the Fe concentration exceeds 0.5, canting of spins occurs either between, or within, the sublattices. The limit of solubility of Fe in the structure appears to occur at, or slightly beyond, the Mn_4FeGe_3 composition.

Introduction

Recently we investigated the magnetic behavior of the system $Mn_{5-x}Fe_xSi_3$, $0 \leqslant x \leqslant 5$, and also used Mössbauer spectroscopy to gain an understanding of the mechanism of substitution of Fe in the two sublattices, 4*d* and 6*g*, of the hexagonal $D8_8$ structure type (*1*). Both end members of the solid solution series have the same structure and thus a complete range of solid solutions could be prepared. The crystal structure of Mn_5Ge_3 is also of the $D8_8$ type but the structure of Fe_5Ge_3 is the hexagonal $B8_2$ type. Both phases are ferromagnetic (*2*, *3*) although there is no agreement as to the moments of Mn in the sublattice sites. The extent of solid solution in the Mn–Fe–Ge system will be limited because of the different structures of the end members. Sozuoka et al. (*4*) and Austin (*5*) investigated the magnetic structure by substituting Mn in the Fe_5Ge_3, $B8_2$, structure. We have investigated the effect of the substitution of Fe in the Mn_5Ge_3, $D8_8$, structure using magnetic and Mössbauer techniques.

Experimental

Iron rod and manganese chips of 99.99% nominal purity and germanium of 99.999% purity were used to prepare the phases $Mn_{5-x}Fe_xGe_3$, $x = 0, 0.5, 1.0, 1.5, 2.0$. All compounds were prepared by melting the elements in the desired proportions in an alumina crucible under 1.25 atmosphere argon pressure in an induction furnace at 1500°C. The reacted material was annealed in an evacuated Vycor tube over a period of 3–4 days at a temperature of 950°C. X-Ray and metallographic examinations were performed and single-phase material having the hexagonal $D8_8$ structure was observed in all cases except at the composition corresponding to $x = 2$, where several phases were present. Lattice constants were determined with a diffractometer using Zr filtered Mo*K* radiation. A least-squares refinement

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TABLE I

CRYSTAL AND MAGNETIC DATA ON $Mn_{5-x}Fe_xGe_3$

Compound	Weiss temperature θ_p (°K)	Curie temperature T_c (°K)	Paramagnetic effective moment[a] μB	Ferromagnetic effective moment[a] (μB/metal atom)	Lattice Constants a (Å)	Lattice Constants c (Å)
Mn_5Ge_3	391.8	304	3.3	2.22	7.17(5)[b]	5.06(2)
$Mn_{4.5}Fe_{0.5}Ge_3$	360.1	318	3.3	2.19	7.13(5)	5.03(3)
Mn_4FeGe_3	371.8	322	3.2	1.88	7.13(8)	5.01(3)
$Mn_{3.5}Fe_{1.5}Ge_3$[c]	365.1	332	2.7	1.46	7.13(9)	4.95(3)

[a] Relative error in μ_{eff} (paramagnetic) and μ_{eff} (ferromagnetic) is 1.6% and 0.5%, respectively.

[b] The number in parentheses is the standard deviation of the last significant figure.

[c] Probably an inhomogeneous phase.

using measured 2θ values yielded the lattice constants shown in Table I. High-temperature X-ray diffraction patterns were obtained in an argon atmosphere using beryllium windows and a platinum sample holder. Temperature was measured with a Pt–Pt, 10% Rh thermocouple. No phase change was observed in high temperature diffraction patterns up to 500°C taken at 100°C intervals.

Paramagnetic susceptibility measurements were made using a Faraday balance and magnetization measurements were made in a vibrating sample magnetometer. Sample temperatures were measured over appropriate ranges either with a copper constantan thermocouple or a carbon resistor. Both sensing devices were in contact with the sample. Mössbauer spectra were determined and analysed using apparatus and programs previously described (*1*).

Mössbauer Results

The Mössbauer spectra of the systems $Mn_{4.5}Fe_{0.5}Ge_3$, Mn_4FeGe_3, and $Mn_{3.5}Fe_{1.5}Ge_3$ are given as a function of temperature in Figs. 1, 2, and 3, respectively, with the appropriate parameters in Tables II and III. At high temperatures, all three compounds show what appears to be a single quadrupole doublet having relatively narrow lines. The computer fit spectra, as well as residual plots give excellent agreement with this assumption. The asymmetry of the high temperature spectrum (Fig. 3a) of $Mn_{3.5}Fe_{1.5}Fe_3$ could be due to either relaxation broadening or residual orientation in the sample. We were unable to determine the spectrum at higher temperatures (using our cryostat) in order to see if the doublet became symmetric. A single quadrupole doublet is not unexpected in the cases of $Mn_{4.5}Fe_{0.5}Ge_3$ and Mn_4FeGe_3 if it is assumed that there is only one kind of iron present, i.e., preferential substitution into one or the other of 4(*d*) or 6(*g*) sites of the $D8_8$ structure of Mn_5Ge_3. The spectra at 78°K are consistent with a single type of iron present. One hyperfine splitting pattern is observed for both $Mn_{4.5}Fe_{0.5}Ge_3$ and Mn_4FeGe_3 although resolution is not complete in the case of the former compound. The presence of combined

TABLE II

MÖSSBAUER PARAMETERS[a] (mm/sec)

Compound	T (°K)	Quadrupole splitting (ΔE)	Isomer shift (δ)	Γ_-	Γ_+	Γ_-/Γ_+	A_-/A_+	H_-/H_+
$Mn_{4.5}Fe_{0.5}Ge_3$	370	0.48	0.35	0.32	0.37	0.88	0.92	1.07
Mn_4FeGe_3	370	0.48	0.36	0.30	0.32	0.96	1.06	0.99
	195	−0.51[b]	0.46					
	78	−0.52[b]	0.53					
$Mn_{3.5}Fe_{1.5}Ge_3$[c]	480	0.43	0.30	0.31	0.33	0.94	0.96	1.04

[a] Obtained by computer fit with respect to 99.99% National Bureau of Standards iron foil; reproducibility of ΔE and δ is ±0.01 mm/sec.

[b] The average value of S_1–S_2, i.e., the shift of the inner 4 lines relative to the outer 2 of a six-line pattern.

[c] Probably an inhomogeneous phase.

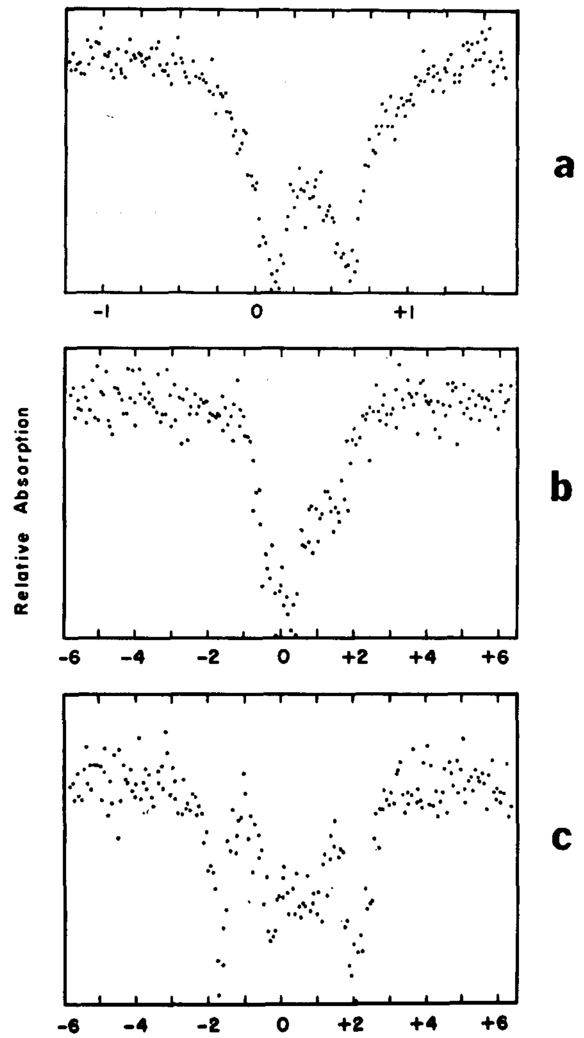

FIG. 1. Mössbauer spectrum of $Mn_{4.5}Fe_{0.5}Ge_3$ at (a) 370°K, (b) 300°K, (c) 78°K.

TABLE III

INTERNAL FIELDS[a]

Compound	Temperature (°K)	Internal field
$Mn_{4.5}Fe_{0.5}Ge_3$	300	83
	78	113
Mn_4FeGe_3	195	144
	78	166
$Mn_{3.5}Fe_{1.5}Ge_3$[b]	370	158
	300	100, 166
	195	145, 176
	78	171

[a] All fields in kG relative to iron foil for which the internal field at 300°K is taken as 330 ± 3 kG.

[b] Probably an inhomogeneous phase.

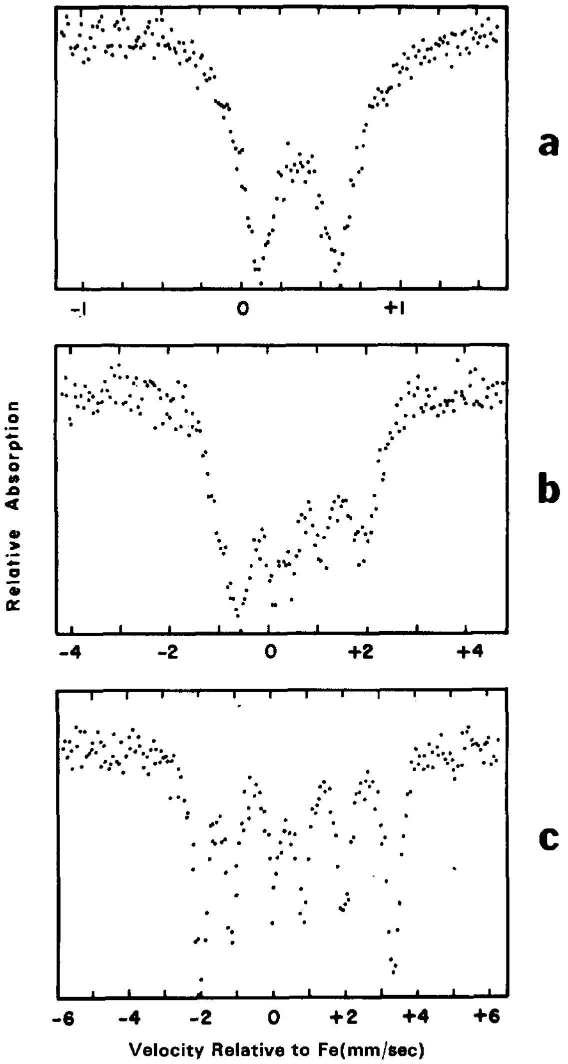

FIG. 2. Mössbauer spectrum of Mn_4FeGe_3 at (a) 370°K, (b) 300°K, (c) 78°K.

quadrupole and magnetic hyperfine interactions is also evident (Fig. 2c).

The Mössbauer spectra of $Mn_{3.5}Fe_{1.5}Ge_3$ over a large temperature range (Fig. 3a–f) clearly show the presence of two magnetic hyperfine patterns. The simplest explanation is the assumption that the sample is inhomogeneous and this is discussed in detail below.

Magnetic Results

The variation of magnetic susceptibility as a function of temperature is shown in Fig. 4 for Mn_5Ge_3, $Mn_{4.5}Fe_{0.5}Ge_3$, Mn_4FeGe_3, and $Mn_{3.5}Fe_{1.5}Ge_3$. Magnetization measurements are shown in Figs. 5 and 6.

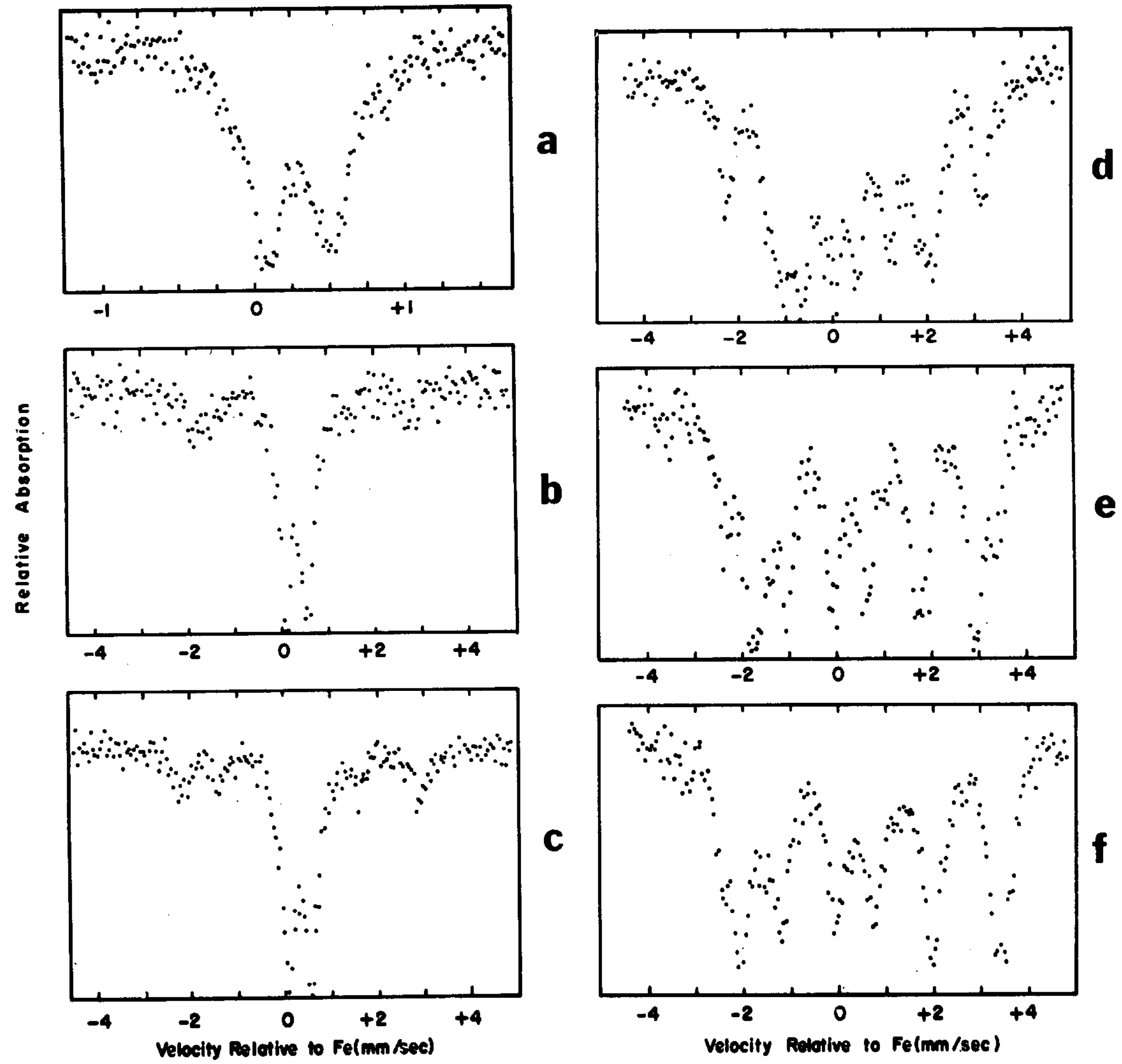

FIG. 3. Mössbauer spectrum of $Mn_{3.5}Fe_{1.5}Ge_3$ at (a) 480°K, (b) 430°K, (c) 370°K, (d) 300°K, (e) 195°K, (f) 78°K.

The susceptibility curves are indicative of ferromagnetic ordering. Weiss temperatures and effective moments in the paramagnetic region are shown in Table I. Ferromagnetic moments at 0°K were calculated by extrapolation of the magnetization versus temperature curves, and are shown in Table I together with the Curie temperatures.

Discussion

Preferential substitution of iron for manganese was observed for the series Mn_5Si_3–Fe_5Si_3 where both end members have the $D8_8$ structure. Correlation of neutron diffraction (*6*), magnetic and Mössbauer (*1*, *7*) results showed the initial substitution to occur exclusively in 4(*d*) sites of Mn_5Si_3 for which the internal field at iron atoms in Mn_4FeSi_3 was ≈ 100 kG at 78°K. While for the present germanium systems the spectra of Figs. 1 and 2 indicate preferential substitution, it is somewhat less certain as to which site, 4(*d*) or 6(*g*), is being occupied first. To our knowledge there are unfortunately no neutron diffraction data for $Mn_{4.5}Fe_{0.5}Ge_3$, and Mn_4FeGe_3 with which to correlate Mössbauer results. Further, the saturation values of internal field are nearly identical (Fig. 3f). Neutron diffraction data (*2*, *9*) show that a lower magnetic moment is associated with the 4(*d*) sites of Mn_5Ge_3 and Mn_5Si_3. It seems reasonable then to assume smaller internal fields with these sites. The rather low initial values of internal field (Table III) therefore suggest occupancy of 4(*d*) sites by iron in

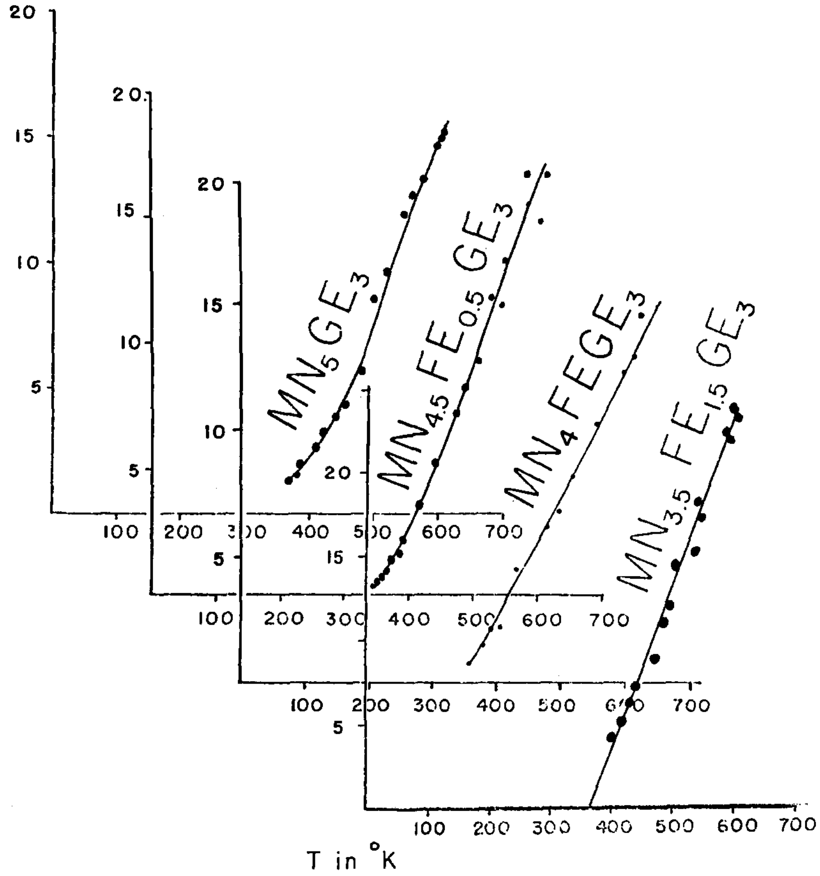

FIG. 4. Inverse magnetic susceptibilities vs. temperature for the $Mn_{5-x}Fe_xGe_3$ phases.

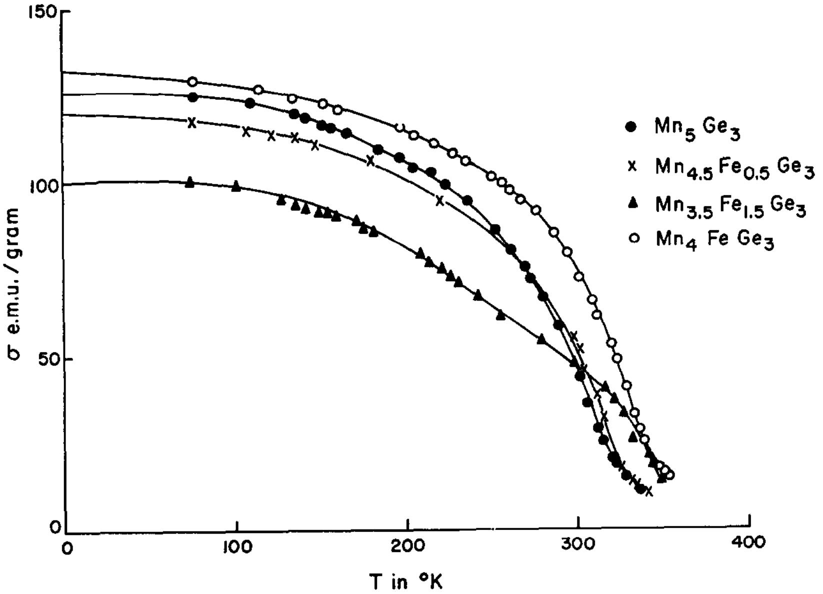

FIG. 5. Magnetization vs. temperature for $Mn_{5-x}Fe_xGe_3$.

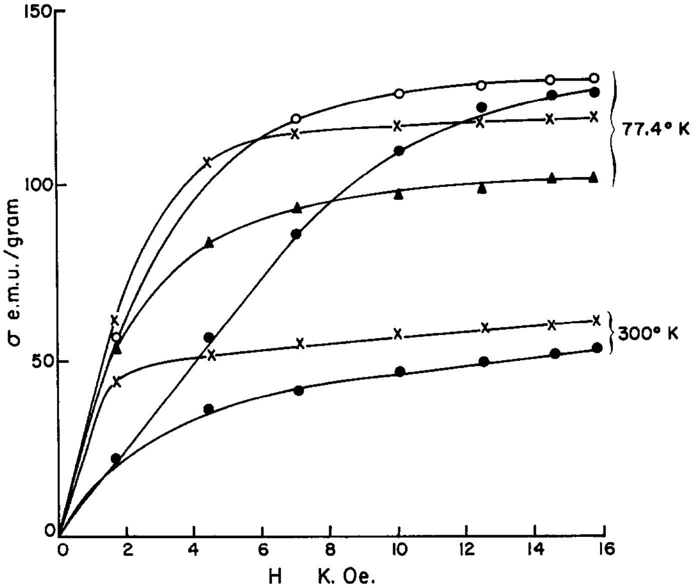

FIG. 6. Magnetization vs. applied field for $Mn_{5-x}Fe_xGe_3$.

$Mn_{4.5}Fe_{0.5}Ge_3$ and Mn_4FeGe_3. This assignment is by no means conclusive but does lead to the most consistent agreement of calculated and observed magnetic results discussed below. It is interesting to note that in a Mössbauer study of the related $B8_2$ system, Fe_5Ge_3, Yamamoto (*8*) associates greatest covalency and lower internal fields with 2(*a*) sites. It is these sites which correlate directly with the 4(*d*) of the $D8_8$ structure.

The Mössbauer spectra of $Mn_{3.5}Fe_{1.5}Ge_3$ (Fig. 3a–f) are difficult to interpret on the basis of a single phase material. Both the high and low temperature behavior is consistent with the possible presence of two slightly different compositions having the $D8_8$ structure. The inhomogeneity of the sample is also indicated by the magnetic measurements as discussed below.

The values of isomer shifts (Table II) are similar to those observed for iron in other group IVB alloys (*10*). On the basis of higher electronegativity, one might expect slightly more positive values of isomer shift for germanides than comparable silicides. The isomer shifts observed in the present study are more positive than those observed for 4(*d*) iron in the Mn_4FeSi_3–Fe_5Si_3 series. However, data for such comparisons are limited. Furthermore, comparisons of isomer shifts as well as hyperfine fields based on electron donating and accepting power of metalloids have been shown to be questionable (*10*).

The magnitudes of the quadrupole splittings (Table II) for the three iron–manganese–germanium systems are comparable to those found for similar silicides and indicate relatively small distortion of electronic symmetry. The quadrupole splittings $\Delta E = e^2 V_{zz} Q/2$ (e = electron charge, V_{zz} = principal component of electrical field gradient tensor, and Q = quadrupole moment), assuming axial symmetry, is related to the shift S_1–S_2 of the inner four lines relative to the outer two of a six-line pattern by the angle θ between V_{zz} and internal field. The relation is $S_1 - S_2 = -\Delta E(3\cos^2\theta - 1)$. For Mn_4FeGe_3 (Fig. 2c) this shift is –0.52 mm/sec while –0.24 mm/sec was observed for Mn_4FeSi_3. The magnitude of S_1–S_2 for Mn_4FeGe_3 is sufficiently close to the high temperature value of ΔE (0.48 mm/sec) so as to make unambiguous determination of the sign of V_{zz} and magnitude of θ difficult using the foregoing relation. This is seen from the fact that for $S_1 - S_2 \leqslant \Delta E$, two values of θ corresponding to different signs of V_{zz} satisfy the relation. For $S_1 - S_2 > E$, one value of θ and V_{zz} satisfy the relation and in the present case implies V_{zz} positive and $\theta \approx 33°$.

We have previously proposed a mechanism for substitution and bonding in the $D8_8$ structure (*1*) and we will use a similar approach for this system to explain the observed changes in the magnetic moment as the iron substitution increases. We shall retain the assumption that covalent bonding exists between the 4(*d*) occupant and the six neighboring silicon atoms and that the cation has a low spin configuration. The environment of the 6(*g*) site consists of 5 Si in the form of a trigonal bipyramid and covalent bonding to the silicon should exist and impart a low spin configuration. In addition, there are 10 other metal atoms nearby, six 6(*g*) atoms and four 4(*d*) atoms and it is postulated that metallic type bonding exists among them. Thus we postulate that the moment on the 6(*g*) site is an average between the moment due to the low spin configuration of the manganese ion and the magnetic moment of metallic manganese. The magnetic measurements reported here can not yield the moments of the respective atoms in the two sites. The two independent measurements of the Mn moments in Mn_5Ge_3 by Forsyth and Brown (*2*) and by Ciszewski (*3*) are in conflict and one must make a choice in order to derive an estimate for the Fe moments. The Mössbauer data give an indication where the substitution of Fe occurs, although it is not unequivocable as in the silicide materials.

Forsyth and Brown (*2*) report a value of 1.7 μB for the 4(*d*) site. This suggests to us that low spin Mn^{+3} is present in this site and we assign a moment of 2 μB to that site. We also assume that the moment for Mn in the 6(*g*) site can be calculated on the assumption of 50% covalent and 50% metallic characters yielding an average moment of 2.5 μB. The reported value from neutron diffraction data is 2.7 μB. Since Mn_5Ge_3 is a ferromagnet, the total calculated moment is 2.30 μB per metal atom. The observed values lie between 2.35 and 2.5 μB per atom and our value of 2.22 μB is probably low due to the failure to saturate the sample (Fig. 6).

Assuming that the initial iron substitution occurs in the 4(*d*) site and that the formula can be written $Mn_3(Mn_{1.5}Fe_{0.5})Ge_3$, then the moment in the 6(*g*) site remains 2.5 μB but the average moment per metal atom in 4(*d*) is 1.75 μB since low spin Fe^{+3} contributes 1 μB. The calculated moment per metal atom is 2.2 μB assuming ferromagnetic alignment of the sublattices, in excellent agreement with the measured value, 2.19 μB.

If continuing Fe substitution occurs in the 4(*d*) site, the formula can be written as $Mn_3(MnFe)Ge_3$ and the 6(*g*) site still has a 2.5 μB moment and the 4(*d*) site has an average moment of 1.50 μB, so that the calculated moment on the basis of ferromagnetic coupling of the sublattices is 2.10 μB/metal atom as compared with the observed value, 1.88 μB.

The lower measured value can be explained on the basis of the magnetic structure of $Mn_{0.9}Fe_{0.9}Ge$ which is an intermediate compound in the Mn–Fe–Ge system. It has the $B8_2$ structure but there is sufficient resemblance between the two structure types so that the knowledge of the magnetic structure of one could be used to explain the behavior of the other. This compound has a noncollinear spin arrangement with a moment of 1.39 μB (*4*). Thus, we interpret our observation of lower than expected moment as due to canting of the spins and a cant angle of 24° between the 4(*d*) and 6(*g*) sublattices will produce the observed moment. Of course, canting of spins within the sublattices may decrease the contribution to the overall moment as well. The present data do not permit a choice between these possibilities.

With iron atoms in excess of 1.0, substitution in the 6(*g*) position most likely occurs and the formula could be written as $(Mn_{2.5}Fe_{0.5})(MnFe)Ge_3$. However, the appearance of the Mössbauer spectra for this composition (Fig. 3b, c) indicate a quadrupolar split line superimposed on a magnetic hyperfine pattern. This suggests one of two alternatives: (a) The two sublattices 6(*g*) and 4(*d*) order magnetically at different temperatures, or (b) the sample consists of at least two phases with different ordering temperatures. For *d* transition metal compounds, alternative (a) is highly unlikely and the second alternative is to be preferred. The magnetic data for $Mn_{3.5}Fe_{1.5}Ge_3$ (Fig. 5) are also reconcilable with (b) since the σ vs. T behavior could be interpreted as due to two or more phases with slightly different Curie temperatures. These phases more than likely have similar structures, such as the $D8_8$, but slightly different compositions. No evidence of another phase was seen in the X-ray diffraction pattern or in metallographic micrographs, as would be the case when materials merely differ in composition. It can be concluded on the basis of the Mössbauer and magnetic evidence that the limit of solubility of Fe in Mn_5Ge_3 occurs between Mn_4FeGe_3 and $Mn_3Fe_2Ge_3$.

Conclusion

From the Mössbauer and magnetic investigation of the phases $Mn_{5-x}Fe_xGe_3$, $x = 0.5$, 1.0 and 1.5, it appears that the initial Fe substitution occurs in the 4(*d*) crystallographic sites of the $D8_8$ structure. When one half of those sites are filled, additional iron may go into the 6(*g*) sites. The postulated magnetic structure is similar to that proposed previously for the $Mn_{5-x}Fe_xSi_3$ phases, although Mössbauer data for the germanide are not as conclusive with respect to the mode of substitution of Fe for Mn in the crystallographically independent sites. Canting of spins apparently takes place between the 4(*d*) and 6(*g*) sublattices, or within the sublattices, when the Fe concentration exceeds 0.5, but the data do not permit a definite choice of models. The limit of solubility of Fe in the structure appears to occur at, or slightly beyond, the Mn_4FeGe_3 composition.

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