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Magnetic phase diagram of the semiordered alloys UFe_xAl_{12-x}

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Single crystals of the ternary semiordered alloys UFe_xAl_{12-x} with $x=3.8$, 4.0, 4.2, 4.5, 4.7, 5.0, 5.5, and 5.8, were prepared, and found to crystallize in the tetragonal $ThMn_{12}$-type structure (space group $I4/mmm$). Studies of monocrystalline and polycrystalline samples of these materials, by ac susceptibility, magnetization, and ^{57}Fe Mössbauer spectroscopy, show two magnetic transitions in the range of $4.0<x\lesssim 4.7$, where only a single transition has been previously reported for polycrystalline materials. These measurements yield the magnetic phase diagram of this system, extending the magnetic structures of single crystal UFe_4Al_8, determined by (unpolarized and polarized) neutron diffraction, of polycrystalline UFe_5Al_7, determined elsewhere by neutron diffraction, and of single crystal $UFe_{5.8}Al_{6.2}$, determined by magnetization. The four magnetic regions, identified in the magnetic phase diagram, and their proposed magnetic structures, are discussed.
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I. INTRODUCTION

The ternary semiordered alloys UFe_xAl_{12-x} have been found to melt congruently, only in the iron-content range of $x=3.8-5.8$ (Refs. 1 and 2). The single-phase materials, obtained from the respective melts, crystallize with the body-centered tetragonal $ThMn_{12}$-type structure, belonging to the space group $I4/mmm$, with occupied $(2a)$, $(8f)$, $(8j)$, and $(8i)$ sites.[1,2] The semiordered-alloy nature of the single-phase UFe_xAl_{12-x} materials in the range of $x=3.8-5.8$ is related to a fixed U occupancy of the $(2a)$ site, and to Fe occupancy of the $(8f)$ site (which is partial in the case of $x<4.0$) and of the $(8j)$ site (for $x>4.0$). The Al atoms occupy all the remaining sites, $(8i)$, $(8j)$, and $(8f)$, the latter for $x<4.0$, with no evidence of vacant sites. The UFe_xAl_{12-x} materials of nominal compositions with $x<3.8$ and with $x>5.8$ contain secondary crystallographic phases.

The only true ternary compound with the $ThMn_{12}$-type structure in the above Fe-content range of the UFe_xAl_{12-x} system, is UFe_4Al_8, with tetragonal lattice parameters of $a=874.9$ pm and $c=503.6$ pm, as established already in 1984 at the W. Trzebiatowski Institute for Low Temperature and Structure Research in Wroclaw (Poland) on polycrystalline[3] and single-crystal[4] samples. In this compound the Al atoms are located on both $(8i)$ and $(8j)$ sites, characterized by position parameters $x(8i)=0.3440$ and $x(8j)=0.2805$, respectively. The Fe atoms are not expected and indeed not found on the aluminum $(8j)$ and $(8i)$ sites.

The magnetic properties of UFe_4Al_8 were studied earlier[5–10] on polycrystalline samples, by ac susceptibility,[5,8] magnetization,[5,8–10] neutron diffraction,[6–8,10] and ^{57}Fe Mössbauer spectroscopy.[8,10] The results were quite different and some of them turned out to be incorrect.[7,8] Magnetic ordering was reported initially around 160 K,[5–7] spin-glass behavior was claimed afterwards below 130 K,[8] and antiferromagnetic (AF) ordering was reported later below 153 K.[10] Based on the various neutron-diffraction data,[6,7,10] the uranium sublattice was claimed to be either nonmagnetic,[6,10] particularly in $B=0$ (Ref. 10), or ferromagnetic (F), with moments along the tetragonal (c) axis.[7] From the same data, the iron sublattice was claimed to be either complex collinear AF with moments along c,[6,7] or AF with moments in the a-b (basal) planes.[10] None of the reports[5–10] turned out to be totally correct.

Later, sizable UFe_4Al_8 single crystals, prepared in a joint project of the Instituto Tecnológico e Nuclear (ITN) and the Institute for Transuranium Elements, Karlsruhe, Germany, enabled better magnetic measurements,[11,12] as well as unpolarized and polarized neutron-diffraction measurements,[13] leading to a reliable description of the magnetic structure at 5 K. These results indicate high anisotropic properties of UFe_4Al_8, with an easy magnetization direction in the a-b (basal) plane,[11] a ferromagnetic ordering of the U moments $[0.47(2)\mu_B$ at 5 K] in the basal plane,[12,13] and a canted AF ordering (16° canting in $B=0$) of the Fe moments $[1.08(2)\mu_B$ at 5 K] in the basal plane, with a ferromagnetic component of $\approx 0.3\mu_B$ aligned parallel to the U-moment direction.[13] These results are consistent with a single-ordering temperature of both U and Fe sublattices, at $\approx$ 150 K.[11–13]

Several semiordered alloys UFe_xAl_{12-x} in the iron-content range of $x=3.8-5.8$ have been studied in the past on polycrystalline samples. Earlier, the materials with $x=4.2$, 4.6, and 4.8 were reported[14] to order ferromagnetically below 145, 230, and 265 K, respectively. Later,[9] the materials with $x=4.2$ and 4.4 were reported to possess a uranium sublattice with F interactions and an iron sublattice with AF interactions, while in the materials with $x=4.6$ and 4.8, only F interactions were found for both sublattices. None of these polycrystalline samples showed more than one magnetic transition.

For the semiordered alloy with $x=5.0$ magnetic ordering, found initially[5] below 268 K, was described afterwards[15] as

F ordering below 261 K. *F* ordering below 280 K of all (U and Fe) moments, perpendicularly to *c*, was confirmed later,[10] by magnetization, neutron-diffraction, and ^{57}Fe Mössbauer-effect measurements. The reported[10] *F*-ordered magnetic moments at 12 K are $0.96(12)\mu_B$ for U in the $(2a)$ site, $1.10(10)\mu_B$ for Fe in the $(8f)$ site, and $1.26(10)\mu_B$ for Fe in the $(8j)$ site, with a total (saturation) moment of $6.6(3)\mu_B$ per formula unit. The partition of Fe atoms among the $(8f)$, $(8j)$, and $(8i)$ sites for $x=5.0$ was reported to be either 2.70, 2.15, and 0.15 (in Ref. 15) or 4.0, 1.0, and 0 (in Ref. 10), respectively.

It is clear from all these contradictory results that better-characterized samples, preferably single crystals, are required in order to make any reliable conclusions on these materials. Indeed, recently we have prepared a single crystal of the semiordered alloy with $x=5.8$ and found that it orders ferromagnetically below 293 K, with a total magnetic moment at 5 K of $10.4\mu_B$ per formula unit.[16] Extrapolation of the U moment in the materials with $x=4.0$ and 5.0, $0.47(2)\mu_B$ and $0.96(12)\mu_B$, respectively, suggests for the material with $x=5.8$ a value higher than $1\mu_B$, leading to an average Fe moment of $\approx 1.5\mu_B$. The partition of Fe atoms among the $(8f)$, $(8j)$, and $(8i)$ sites is 4.0, 1.4(1), and 0.2(1), according to the x-ray-diffraction data, or 4.08(8), 1.76(8), and 0.00(8), according to the more-reliable neutron-diffraction data, respectively. Both techniques indicated that the excessive 1.8 atoms of Fe go mainly to the $(8j)$ site.

We present here the study of several single-crystal UFe_xAl_{12-x} materials in the congruent melting range of $x=3.8-5.8$, by ac susceptibility, by magnetization, and by ^{57}Fe Mössbauer-effect measurements, and propose a magnetic phase diagram of the UFe_xAl_{12-x} system in this Fe-content range.

II. EXPERIMENTAL DETAILS

Bulk charges for the single-crystal growth of the ternary UFe_xAl_{12-x} materials of nominal compositions $x=3.8$, 4.0, 4.2, 4.5, 4.7, 5.0, 5.5, and 5.8, were prepared by repeated melting in an induction furnace of stoichiometric amounts of uranium (depleted), iron, and aluminum with purities of at least 99.9%.

Single crystals of the above materials were grown from the bulk charges in an induction furnace with a levitation cold crucible by the Czochralski method, using a tungsten needle as a seed. A pulling rate of 2 cm/h and a rotation rate of 15 rpm were employed as described earlier.[1] Single crystals were selected from the materials pulled from the melt, for the magnetization measurements, while the remaining parts of these pulled materials were used as polycrystalline samples for ac susceptibility, and, after crushing, for ^{57}Fe Mössbauer-effect measurements.

Single-crystal x-ray measurements were used for the determination of the lattice parameters at room temperature (RT). Small single crystals, removed from the polycrystalline materials, were glued on the top of a glass fiber and transferred to a goniometer mounted on an Enraf-Nonius CAD-4 diffractometer with graphite monochromatized Mo $K\alpha$ radiation ($\lambda=71.073\,\mathrm{pm}$). The least-squares refinement of the 2θ values of 25 strong and well-centered reflections from the various regions of the reciprocal space in the range $16.3° <2\theta< 38.2°$ was used to obtain the tetragonal unit-cell parameters.

ac susceptibility measurements ($f=95\,\mathrm{Hz}$, $B_{\max}\approx 0.2\,\mathrm{mT}$) were done on materials pulled from their melts in the temperature range 12–300 K using a mutual inductance technique.

Magnetization measurements were performed on oriented UFe_xAl_{12-x} single crystals with approximate dimensions $1\times 1\times 1\ \mathrm{mm}^3$, using a superconducting quantum interference device magnetometer (Quantum Design) with applied magnetic fields along the *a* and *c* axes, which in the cases of UFe_4Al_8 and $UFe_{5.8}Al_{6.2}$ are the easy and hard magnetization directions, respectively. The magnetization was measured under magnetic fields, low (LF, 5–20 mT) and medium (MF, 50–100 mT), in the temperature range of 10–300 K, both after zero-field-cooling (ZFC) and field-cooling (FC) procedures.

^{57}Fe Mössbauer-effect measurements were performed on materials pulled from their melts, crushed into polycrystalline samples, and pressed together with Lucite powder into perspex holders, in order to obtain homogeneous and isotropic Mössbauer absorbers containing ~5 mg/cm^2 of natural iron. The ^{57}Fe Mössbauer-spectroscopy results were obtained in the transmission mode using a constant-acceleration spectrometer and a 25 mCi ^{57}Co source in Rh matrix. The velocity scale was calibrated using an α-Fe foil at RT. Spectra were collected at several temperatures between 300 and 5 K. Low-temperature spectra were obtained using a flow cryostat with temperature stability of ±0.5 K. The spectra were fitted to Lorentzian lines using a modified version of the nonlinear least-squares computer method of Stone.[17] The fitting procedure is described in detail elsewhere.[18]

III. RESULTS

The crystallographic structure of all studied ternary semiordered alloys UFe_xAl_{12-x} is consistent with the $I4/mmm$ space group. It was refined to be the $ThMn_{12}$-type crystallographic structure for $x=4.0$ (UFe_4Al_8), $x=5.0$, and $x=5.8$, and all other alloys probably adopt the same structure. Scanning-electron-microscope examination of these samples indicate single-phase materials with no sign of impurity phases. The RT lattice parameters found by the x-ray measurements are listed in Table I.

The ac susceptibility measurements show single magnetic transitions for the UFe_xAl_{12-x} semiordered alloys with $x=3.8$, 5.0, 5.5 and 5.8, the observed peaks on the ac-susceptibility versus temperature curves being quite sharp. Two magnetic transitions are observed in the semiordered alloys with $x=4.2$, 4.5, and 4.7. The relative height of the two ac susceptibility peaks varies with composition. For the $x=4.2$ material the higher-temperature peak is stronger by a factor of 1.4 from the lower-temperature peak. For $x=4.5$ and 4.7 the higher-temperature peak is much stronger (the ratio increasing to ≈4). The samples with nominal Fe content $x=4.0$ show essentially a single ac susceptibility peak. Representative ac susceptibility curves are shown in Fig. 1(a) for the $x=3.8$ material (one transition), and in Fig. 2(a) for the $x=4.2$ material (two transitions). The magnetic transition temperatures are listed in Table I.

Magnetization measurements show the same magnetic

TABLE I. RT lattice parameters and (zero-field) magnetic transition temperatures as functions of the iron content *x* in single crystals of the semiordered alloys UFe_xAl_{12-x}.

x	*a* (pm)	*c* (pm)	Transition temparatures (±5 K). (K)		
3.8	873.5(1)	502.8(1)		155	
4.0	874.0(1)^a	503.6(1)^a		148^a	
4.2	872.31(4)	502.79(3)	150		178
4.5	869.7(2)	502.9(2)	130		217
4.7	867(1)	502.4(5)	105		228
5.0	868.51(3)	501.67(3)		278	
5.5	867.66(5)	501.33(4)		287	
5.8	867.44(3)^b	501.42(3)^b		293^b	

^{a}Already reported in Ref. 13.
^{b}Already reported in Ref. 16.

transitions observed by ac susceptibility. In the LF measurements transitions appear on both the ZFC and the FC curves, when measured along the easy-magnetization direction *a* (or *b*), perpendicular to the *c* axis. A single magnetic-ordering transition is observed for the material with $x=3.8$ [Fig. 1(b)] and for UFe_4Al_8 ($x=4.0$),[11] in the latter case even for those samples exhibiting split ac-susceptibility peaks. The upper magnetic transitions for the semiordered alloys with $x=4.2$ [Fig. 2(b)], 4.5, and 4.7, are rather steep, first-order-like, in the case of LF ($B=5-10$ mT) values. In medium fields ($B=50$ or 100 mT) these transitions become rounded, similar to the LF single transition in UFe_4Al_8 ($x=4.0$) (Ref. 11) and in the material with $x=5.8$ (Ref. 13). For the semiordered alloys with $x=5.0$, 5.5, and 5.8 (Ref. 13), sharp single transitions are observed.

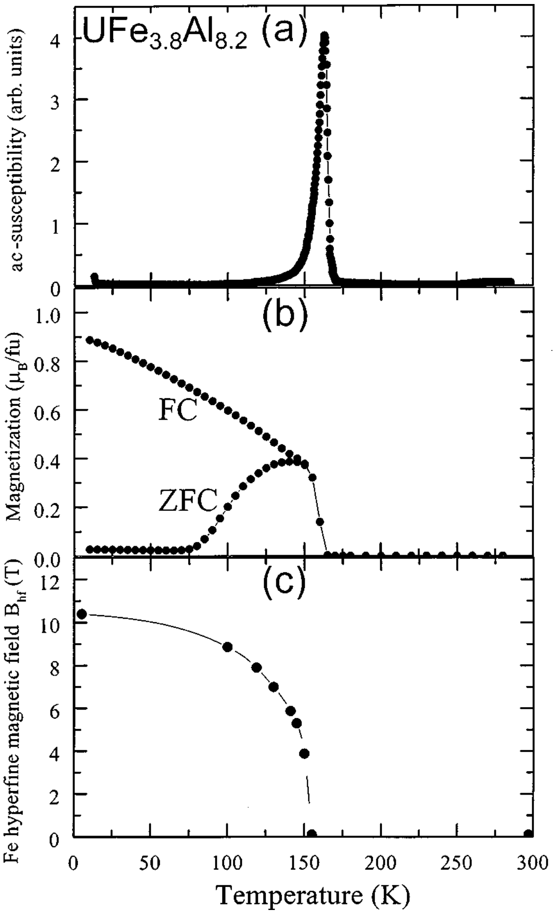

FIG. 1. Magnetic measurements on the semiordered alloy $UFe_{3.8}Al_{8.2}$ as functions of temperature: (a) ac susceptibility of a polycrystalline material (pulled from the melt); (b) ZFC and FC magnetization of a single crystal, in a magnetic field $B=5$ mT, applied along an easy direction; (c) hyperfine magnetic field at the ^{57}Fe nuclei in the ($8f$) site, deduced from the Mössbauer spectra of a powdered sample of material pulled from the melt. A single magnetic transition is evidenced at 155±5 K.

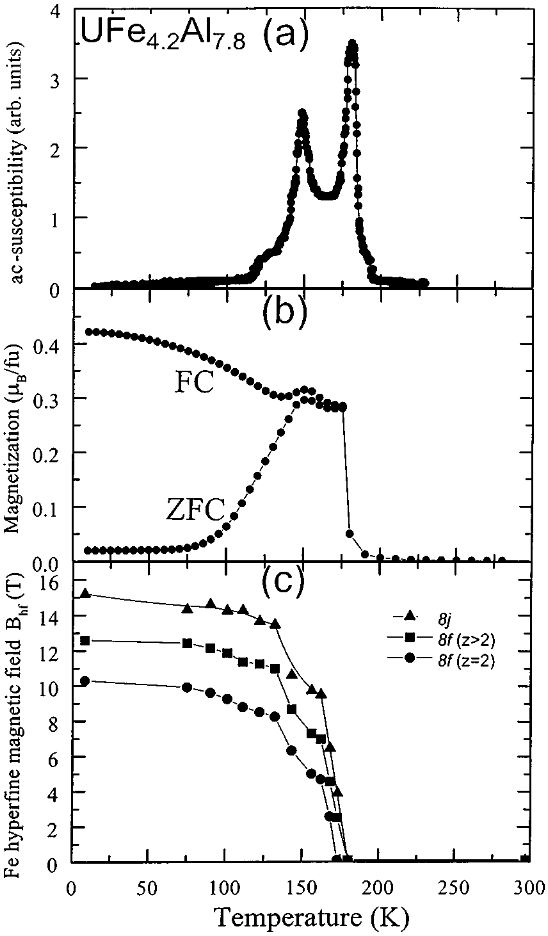

FIG. 2. Magnetic measurements on the semiordered alloy $UFe_{4.2}Al_{7.8}$ as functions of temperature: (a) ac susceptibility of a polycrystalline material (pulled from the melt); (b) ZFC and FC magnetization of a single crystal, in a magnetic field $B=5$ mT, applied along an easy direction; (c) hyperfine magnetic fields at the ^{57}Fe nuclei in the sites ($8f$) with $z=2$, ($8f$) with $z>2$, and ($8j$) with $z\geqslant 4$, deduced from the Mössbauer spectra of a powdered sample of material pulled from the melt. Two magnetic transitions are evidenced at 150±5 and 178±5 K.

The ^{57}Fe Mössbauer spectra in the paramagnetic state of UFe_4Al_8 and $UFe_{3.8}Al_{8.2}$ consist of symmetrical doublets. In these materials the iron atoms occupy a single crystallographic site, ($8f$), and therefore only one doublet is expected.

The ^{57}Fe Mössbauer spectra obtained for UFe_4Al_8 in the ordered state, down to 5 K, are accounted for by a single magnetic sextet.[10,18] The ^{57}Fe Mössbauer spectra obtained for other UFe_xAl_{12-x} semiordered alloys in the ordered state, can only be fitted assuming that the magnetic hyperfine fields of the Fe atoms depend on the crystallographic site (for $x > 4.0$) and on the number (z) of Fe nearest neighbors, as described in detail elsewhere.[18] Assuming a random distribution of Fe and Al atoms on the $(8f)$ site in $UFe_{3.8}Al_{8.2}$, around 10% of the Fe atoms have only one Fe nearest neighbor (NN), while the remaining 90% have two Fe NN's, as in UFe_4Al_8. Therefore, one might expect that more than one sextet would be needed to fit the spectra of $UFe_{3.8}Al_{8.2}$ in the ordered state. Nevertheless, these spectra show that all the Fe nuclei have the same magnetic hyperfine field B_{hf} regardless of the number of Fe NN's, with a reduced value as compared to B_{hf} in UFe_4Al_8. On the other hand, a small fraction ($\leqslant 3\%$) of paramagnetic Fe atoms are probably present down to 5 K. This may be due to isolated clusters of uncorrelated Fe atoms. The temperature dependence of B_{hf} estimated for the large majority of magnetically ordered Fe atoms in $UFe_{3.8}Al_{8.2}$ [as shown in Fig. 1(c)] indicates a single magnetic transition at ≈155 K, consistently with the other magnetic measurements.

In the semiordered alloys UFe_xAl_{12-x} with higher Fe content ($4.2 \leqslant x \leqslant 5.8$), as iron atoms are present on two crystallographic sites, $(8f)$ and $(8j)$, the spectra in the paramagnetic state are the sums of more than one symmetrical doublet, as discussed elsewhere.[18] In the ordered state, there is a distinction between iron atoms on the $(8f)$ and $(8j)$ sites, as well as between $(8f)$ iron atoms with different number (z) of iron NN's.[18] Actually, we have $(8f)$ iron atoms with $z=2$, as in UFe_4Al_8, and $z=3$ and 4, as in the cases of higher Fe contents, together with $(8j)$ iron atoms with 4 or more iron NN's. A binomial distribution is used for calculating the probability of the possible NN configurations of the Fe atoms arising from the random distribution of the Fe and Al atoms on the $(8j)$ site. Several (more than one) sextets, with relative areas consistent with these probabilities, are fitted to the spectra. The magnetic hyperfine fields B_{hf} are found to increase, and the isomer shifts δ are found to decrease, with the number of Fe NN's of the Fe atoms on each crystallographic site. This model, described elsewhere,[18] and formerly applied only to the spectra obtained at 5 K, is now confirmed for the spectra taken for all the semiordered alloys in the whole temperature range of the ordered magnetic state down to 5 K.

The temperature dependence of B_{hf} of the Fe nuclei on the various sites in $UFe_{4.2}Al_{7.8}$ [Fig. 2(c)] indicates two magnetic transitions in this material, at ≈178 K and at 143–154 K, consistently with the other magnetic measurements on this material. If similar temperature dependences are assumed for all the B_{hf} and the corresponding Fe magnetic moments, a discontinuity in the Fe-moment versus temperature curves seems to occur around 155 ± 5 K. This discontinuity is less pronounced for Fe on $(8f)$ sites. The situation is described below 155 ± 5 K by a curve $m_L(T)$, which extrapolates to a lower moment at $T=0$, and above 155 ± 5 K by a curve $m_H(T)$, extrapolating to a higher moment at $T=0$, so that $m_L(T=0) < m_H(T=0)$. A similar behavior of $B_{hf}(T)$, progressively less pronounced with increasing Fe content, is observed in $UFe_{4.5}Al_{7.5}$ and $UFe_{4.7}Al_{7.3}$.

The magnetic hyperfine fields at 5 K, $B_{hf}(5\,K)$, for the various sites, vary with the Fe content x. In the case of UFe_4Al_8 ($x=4.0$), with the single Fe site $(8f)$, in which each iron atom has two iron NN's, we obtain $B_{hf}(5\,K) = 11.0\,T$. For $x=4.2$ only 95% of the Fe atoms are on the $(8f)$ site, with only 77% having two iron NN's, while 5% of the Fe atoms are on the $(8j)$ site.[18] On the average, we obtain $B_{hf}(5\,K) = 11.1$ T, similar to the value for $x=4.0$. The ratio of the number of Fe atoms on the $(8f)$ and $(8j)$ sites is 89:11 for $x=4.5$, 80:20 for $x=5.0$, and 69:31 for the final composition, $x=5.8$. The average $B_{hf}(5\,K)$ value goes down slightly, to 10.3 T, for $x=4.5$, and then rises to 12.0 T for $x=5.0$, and finally to 12.5 T for $x=5.8$. Our average value for $x=5.0$ is in agreement with the one previously reported[10] for a polycrystalline sample.

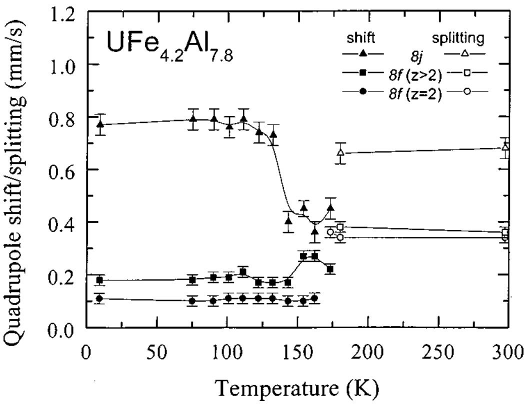

FIG. 3. Temperature variation of the quadrupole shift/quadrupole splitting of the ^{57}Fe Mössbauer spectra (in zero applied magnetic field) in the semiordered alloy $UFe_{4.2}Al_{7.8}$. Shifts/splittings are shown for iron atoms on the sites $(8f)$ with $z=2$, $(8f)$ with $z>2$, and $(8j)$ with $z \geqslant 4$, the latter two also indicating the two transitions seen in the temperature dependence of the hyperfine field [Fig. 2(c)]. At 175 K the Fe atoms on the $(8f)$ site with $z=2$ are paramagnetic.

The $UFe_{4.2}Al_{7.8}$ quadrupole shifts ϵ of the Fe atoms on the $(8f)$ site in the entire temperature range of the ordered state are similar, within the experimental error (Fig. 3). However, the ϵ values of the Fe atoms on the $(8j)$ site show an abrupt change between 143 and 154 K. Although the uncertainties in these ϵ values are large due to the low intensity of the corresponding sextets, they are lower than the observed change in the ϵ values. No crystal-structure transition is expected in this temperature range, since the crystallographic structures at RT and at 5 K are the same for UFe_4Al_8 (Ref. 13), UFe_5Al_7 (Ref. 10), and $UFe_{5.8}Al_{6.2}$ (Ref. 16). A change in the directions of the magnetic moments of the Fe atoms, between 143 and 154 K, would explain such an effect on the the ϵ values. A similar behavior of the ϵ curves, progressively less pronounced with increasing Fe content, is observed in $UFe_{4.5}Al_{7.5}$ and $UFe_{4.7}Al_{7.3}$.

The transition temperatures in the semiordered alloys UFe_xAl_{12-x} (Table I), as obtained from the ac-susceptibility curves, plotted as function of the Fe content x (Fig. 4), form the basis of the magnetic phase diagram of this system in zero applied magnetic field. The four magnetic regions, $M1-M4$, indicated in this magnetic phase diagram (Fig. 4), and the proposed magnetic structures (see later, in Fig. 5), are discussed in the next section.

IV. DISCUSSION

A small variation of the tetragonal-lattice parameters with the number of Fe atoms per formula unit x is observed in the

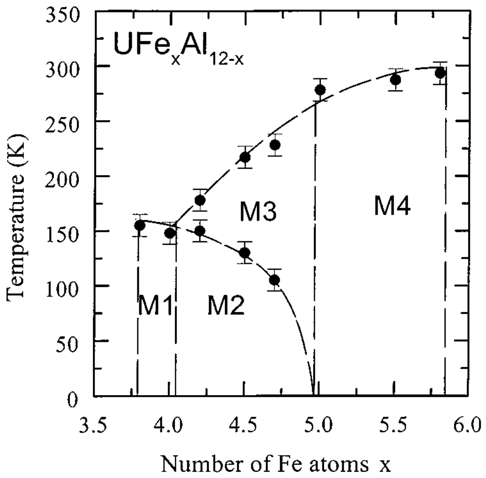

FIG. 4. Magnetic phase diagram, in zero applied magnetic field, of the semiordered alloys UFe_xAl_{12-x}. The only magnetic structures determined by neutron diffraction (at $T\approx5$ K) are of single crystal UFe_4Al_8 (Ref. 13) characterizing the $M1$ region, and of polycrystalline UFe_5Al_7 (Ref. 10) characterizing the $M4$ region. The magnetic structure of single crystal $UFe_{5.8}Al_{6.2}$ was obtained by magnetization measurements (Ref. 16). Basal-plane magnetic-moment arrangements, proposed through the four regions, are described in Fig. 5.

semiordered alloys UFe_xAl_{12-x} (Table I). Over the entire range of congruent melting, $x=3.8$–5.8, the parameter *a* decreases by 0.8%, while the parameter *c* decreases by merely 0.5%. Almost the entire decrease occurs between $x=4.0$ and $x=4.7$. For higher *x* values the variation of the lattice parameters is not significant.

Bulk measurements, performed on the semiordered alloys UFe_xAl_{12-x}, ac susceptibility on polycrystalline materials and magnetization of single crystals, as well as the microscopic ^{57}Fe Mössbauer-effect measurements, yielded a new insight into their magnetic properties. In these materials a composition range with two consecutive magnetic transitions (shown in Table I and Fig. 4) is evidenced by all three investigation methods (Fig. 2). In this iron-content range ($4.0<x\lesssim4.7$) the initial magnetic ordering, from the paramagnetic into the $M3$ region (Fig. 4), has a strong ferromagnetic component indicated by the steepness of the transition observed in ac susceptibility (first-order-like) and by the size and temperature dependence of the magnetization. The second transition, from the $M3$ to the $M2$ region (Fig. 4), corresponding to a change in the iron magnetic moment to lower values, can be considered as having a reduced ferromagnetic character.

The four magnetic regions ($M1-M4$) of the magnetic phase diagram of the semiordered alloys UFe_xAl_{12-x} (Fig. 4) are obtained by the three types of measurements done on these materials. The region $M1$ extends from $x=3.8$ to $x=4.0$, while the $M4$ region extends from *x* slightly below 5 up to $x=5.8$. The $M2$ and $M3$ regions occur, at low and high temperature, respectively, between the $M1$ and $M4$ regions.

The only magnetic-structure determinations made by neutron diffraction (at $T\approx5$ K) are those of UFe_4Al_8, on a single crystal,[13] characterizing the $M1$ region, and of UFe_5Al_7, on a powder sample,[10] characterizing the $M4$ region. These measurements, as well as the magnetization study of single crystal $UFe_{5.8}Al_{6.2}$,[16] indicate *F* ordering of the U moments in the basal planes, along the *a* direction, in both $M1$ and $M4$ regions.

In the $M1$ region the Fe moments, existing only on the $(8f)$ site, have the canted AF structure, actually observed for UFe_4Al_8.[13] The ^{57}Fe Mössbauer results for the quadrupole shift show no change with temperature and stay almost constant up to the ordering temperature, indicating that the magnetic structure hardly changes with temperature. However, in Fe-deficient materials, as $UFe_{3.8}Al_{8.2}$, paramagnetic iron atoms also exist, corresponding to the replacement by Al atoms of one or two of the Fe NN's, as evidenced in the ^{57}Fe Mössbauer measurements. On the contrary, in the $M4$ region all Fe moments, on both $(8f)$ and $(8j)$ sites, have *F* ordering along the same direction of the U moments.

It is reasonable to believe that the U moments in the $M2$ and $M3$ regions have *F* ordering in the basal plane, as in the extreme regions $M1$ and $M4$. The size of the U moment can be considered to vary across the entire congruent melting range, $3.8\leqslant x\leqslant5.8$, around the values of $0.47(2)\mu_B$ and $0.96(12)\mu_B$, measured for the materials with $x=4.0$ and 5.0, respectively.

Assuming *F* ordering of the U moments in all four region, all magnetic phases are related to the various magnetic structures of the Fe sublattices. In the absence of neutron-diffraction measurements in the $M2$ and $M3$ regions of the magnetic phase diagram, the assignment of magnetic structures for the Fe moments is somewhat speculative; a spin-glass-like behavior is not expected, given the magnetic structures determined for $x=4.0$ (Ref. 13) and $x=5.0$ (Ref. 10)

Based on our experimental results, the following proposal is made to describe these structures. The border line between the $M1$ and $M2$ regions, at *x* above 4.0, is established as a result of the occupation of the $(8j)$ site by Fe atoms. The random nature of this occupation excludes any long-range AF ordering of these moments, and leads to the alignment of these $(8j)$-site iron moments along the already established direction of *F* ordering of the U moments. The alignment of the moments on the $(8j)$ site increases with the Fe content *x* leading to a collinear ferromagnetism in the $M4$ region. Considering for the $M2$ region a canted AF ordering of the $(8f)$ iron moments, as detected for UFe_4Al_8, it is reasonable to believe that the increase of the molecular field on the $(8j)$ site affects this canting angle, thereby increasing gradually the corresponding *F* component, with respect to the value determined in UFe_4Al_8 ($\approx0.3\mu_B$). At the border of the $M4$ region, for *x* slightly below 5, all the iron moments acquire the *F* ordering, and along with the *F* ordering of the uranium moments they form the ferromagnetic $M4$ region.

The ^{57}Fe Mössbauer results for the quadrupole shift indicate that for any Fe content *x* the arrangements of the iron moments on the $(8f)$ site with two Fe NN's do not change with temperature up to the higher transition (see Fig. 3). This result indicates that the $(8f)$ canted AF ordering is present along the $M3$ region. However, the arrangements of iron moments on the $(8f)$ site with three or more Fe NN's and on the $(8j)$ site change with temperature (see Fig. 3), and

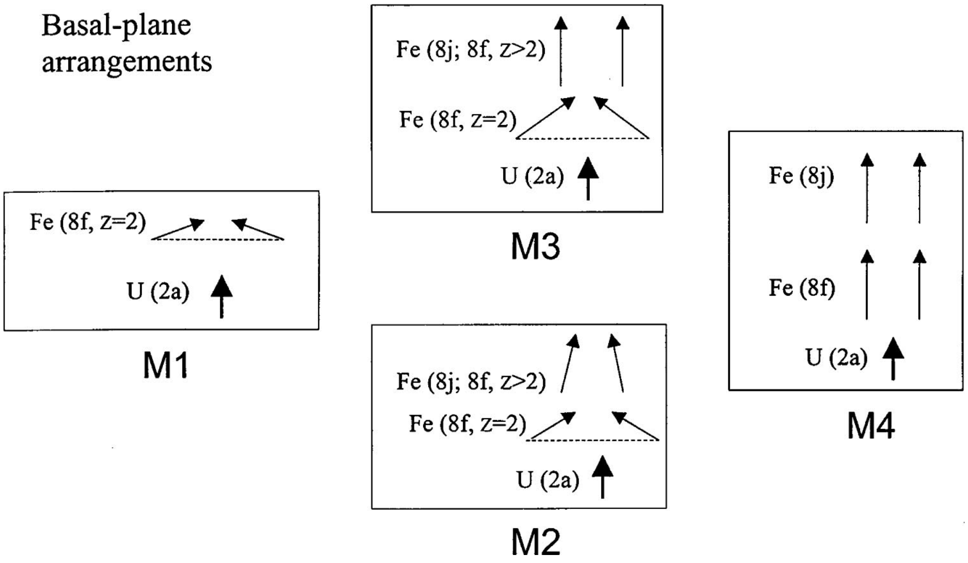

FIG. 5. Proposed basal-plane magnetic-moment arrangements in the four regions of the magnetic phase diagram of the semiordered alloys UFe_xAl_{12-x} (Fig. 4), based on ac susceptibility, magnetization, and ^{57}Fe Mössbauer spectroscopy measurements. The two iron-moment regimes, $m_L(T)$ and $m_H(T)$, are distinguished by the size of the arrows. The canting angle in the $M2$ and $M3$ regions is a representative one.

indeed increase on raising temperature from the $M2$ region into the $M3$ region.

If similar variations with x are assumed for B_{hf} and the corresponding Fe magnetic moments, the ^{57}Fe Mössbauer data suggest that for any Fe content x from 4 to 5, there is an increase of the Fe moments on all sites [see Fig. 2(c)], on raising the temperature across the border from the $M2$ to the $M3$ region, the latter having a stronger F character. One can assume that the observed temperature variation corresponds to an increase of the canting angle with temperature toward F ordering, in the border crossing from the $M2$ to the $M3$ region. The increase of canting in this border crossing, toward a collinear F ordering, applies also to the F component of the Fe moments on the $(8j)$ site (see Fig. 3). From the average $B_{\mathrm{hf}}(5\,\mathrm{K})$ results, the same increase is expected in crossing the border from the $M2$ into the $M4$ region. As mentioned above, in the $M4$ region all the Fe moments are assumed to have a collinear F ordering.

The lower border of the $M1$ region, at $x=3.8$, and the upper border of the $M4$ region, at $x=5.8$, are related to the congruent melting range. The upper border of the $M1$ region, at $x=4.0$, is set on by the initial occupation of the $(8j)$ site by iron moments. The lower border of the $M4$ region, at x slightly below 5, is determined by the establishment of full ferromagnetic order. The exact border line between the $M2$ and $M3$ regions, especially near $x=5.0$, is still not known precisely. As this border involves higher Fe moments in the higher-temperature $M3$ region, it is probably related to the complex band structure and to the partial itinerant nature of iron in the present materials.

The proposed basal-plane magnetic-moment arrangements in the UFe_xAl_{12-x} system of semiordered alloys (Fig. 4), are described schematically in Fig. 5. The general feature of this description involves a transition of Fe magnetic moments from the regime of lower moments, $m_L(T)$, in the $M1$ and $M2$ regions to the regime of higher moments, $m_H(T)$, in the $M3$ and $M4$ regions. The canting angle α of the Fe moments on the $(8f)$ site, having two iron NN's, varies between 16° in the $M1$ region and 90° (collinear ferromagnetism) in the $M4$ region. It is still not clear if the canting angle α varies smoothly across the borders at $x=4.0$ and at x slightly below 5. The canting angle of the Fe moments on the other sites throughout the $M2$ region, or their F components, are still unknown. This angle, and therefore also the F components, both increase upon crossing into the $M3$ region.

In conclusion, the ac-susceptibility, magnetization, and ^{57}Fe Mössbauer data presented above indicate a complex magnetic phase diagram of the semiordered alloys UFe_xAl_{12-x}, with two transitions in the range between $x=4.0$ and x slightly below 5, as summarized in Fig. 4. However, in the absence of neutron-diffraction data, the interpretation of the $M2$ and $M3$ regions is rather tentative. Neutron-diffraction measurements on single crystals in these regions, and further magnetization studies, now under planning, are expected to confirm the proposed interpretation.

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