Journal of Alloys and Compounds, 191 (1993) 213–217
JALCOM 497

^{57}Fe Mössbauer effect study of the $UFe_{10-x}Al_xSi_2$ system

F. G. Vagizov*, H. Drulis, W. Suski and A. V. Andreev**
Polish Academy of Sciences, W. Trzebiatowski Institute of Low Temperature and Structure Research, P.O. Box 937, 50–950 Wrocław 2 (Poland)

(Received July 30, 1992)

Abstract

^{57}Fe Mössbauer spectroscopy has been used to study the $UFe_{10-x}Al_xSi_2$ system in the temperature range 14–295 K for $x \leq 3.0$ (single-phase region). The Mössbauer spectra provide values of the hyperfine fields and their deconvolution gives information about the occupancy of the individual crystallographic positions 8f, 8j and 8i by the Fe atoms. The data obtained explain the change in the anisotropy character for $x = 2$ and provide evidence for the U sublattice contribution to the magnetic ordering. The results obtained are discussed in comparison with earlier magnetic measurements in terms of geometrical factors.

1. Introduction

$UFe_{10}Si_2$ is an actinide analogue of the rare earth, $ThMn_{12}$-type compounds which seem to be promising magnetic materials. Also, the U compound exhibits high values of spontaneous magnetization and the Curie temperature. The Curie temperature is equal to 653 K [1–4] and can even be increased up to 750 K by partial substitution of Co for Fe [5, 6]. The serious disadvantage of $UFe_{10}Si_2$ is its lack of measurable remanence. However, the $UFe_{12-x}Al_x$ system, which also adopts the $ThMn_{12}$-type tetragonal structure and exists in a single-phase form in the range composition $6 < x < 9$, shows a considerable remanence (see ref. 7 and references cited therein, as well as refs. 8 and 9). Therefore, we have tried to combine both systems. Our preliminary investigations showed that an admixture of Al either to $UFe_{10}Si_2$ or to $U(Fe, Co)_{10}Si_2$ does not increase the remanence considerably [5]. The subsequent, more detailed examination of the $UFe_{10-x}Al_xSi_2$ system [10] provided information that the homogeneity range only extends up to $x \simeq 3$. The magnetic moment and the Curie point decrease linearly with increasing Al content, whereas the uniaxial magnetocrystalline anisotropy is reduced and the compounds with $x > 2$ have basal-plane-type anisotropy.

The compounds with the $ThMn_{12}$-type structure (14/*mmm*) have unit cells with four non-equivalent crystallographic positions: the U atoms occupy the position of the 2a type, and the Fe, Al and Si atoms are distributed over the 8f, 8i and 8j positions. In $UFe_{10}Si_2$, it is known that the Si atoms occupy 8f and 8j sites, whereas the 8i position is mostly occupied by the Fe atoms [6, 11]; such a distribution of the Fe atoms is very important in determining the magnetic properties of $UFe_{10}Si_2$ and its derivatives. This importance results from the fact that the Fe atoms located in the 8i positions have the largest number of nearest neighbour (nn) Fe atoms and the largest Fe–Fe separation, which creates the strongest ferromagnetic exchange interactions within the Fe 8i sublattice. As one can see from an inspection of the $ThMn_{12}$-type structure, this sublattice is also responsible for the uniaxial anisotropy of the material. Therefore, to understand the magnetism of the $UFe_{10-x}Al_xSi_2$ system, the distribution of hyperfine fields corresponding to the substitution of the Fe atoms by the Al atoms determined from the ^{57}Fe Mössbauer experiment is very important.

2. Experimental details

The $UFe_{10-x}Al_xSi_2$ alloys were obtained by melting the components (U 99.9% and Fe, Al and Ti 99.99% purity) in an arc furnace under an Ar protective atmosphere, and annealing them at 900 °C for two weeks.

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*Permanent address: Physicotechnical Institute, Russian Academy of Sciences, 420029 Kazan, Sibirskii Trakt 10/17, Russian Federation.

**Permanent address: Permanent Magnets Laboratory, Institute of Physics and Applied Mathematics, Ural State University, 620083 Ekaterinburg, Russia. Present address: Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan.

0925-8388/93/$6.00

The components were used in stoichiometric amounts, except for uranium which was used in a quantity 1% over the stoichiometric amount.

The Mössbauer measurements were carried out using a conventional constant acceleration spectrometer (Polon) with ^{57}Co in a Cr matrix as the source from 14 to 295 K. The velocity scale was calibrated using an α-Fe absorber at room temperature. To examine the possible spin reorientation transition, we used powders with a particle size of about 45 μm mixed with 15% Si oil and aligned at room temperature in a magnetic field of 1.2 T.

3. Results and discussion

The X-ray examination exhibited a single phase with the $ThMn_{12}$-type structure for the compounds with $x<3$. In the alloys with $x>3$, large amounts of foreign unidentified phases are observed. Although the boundary compound $UFe_7Al_3Si_2$ exhibits traces (5% or less) of a second phase, it is considered here to belong to the homogeneity range of the investigated system. As has been reported previously [10], the increase in both the lattice parameters with increasing Al concentration reflects the larger size of Al atoms comparing with those of Fe. A considerable deviation from Vegard's law suggests the preferential occupation of different crystallographic positions by Fe, Al and Si, as has been established in the present Mössbauer experiment.

In Fig. 1, the Mössbauer spectra for $UFe_{10-x}Al_xSi_2$ alloys with $0 \leq x \leq 2.5$ obtained at 14 K are presented. The experimental spectra, as in previous papers [6, 11, 12], are approximated by three sextets resulting from the three non-equivalent positions of the Fe atoms, *i.e.* 8f, 8i and 8j. As discussed in the introduction, the sextets corresponding to the 8i positions exhibit the largest hyperfine field, whereas, because of the shortest distance between the Fe atoms in the 8f positions, the ferromagnetic interactions between the Fe atoms are weakened by the antiferromagnetic interactions; the corresponding sextet reflects the weakest hyperfine field. Such a correspondence of the sextets to the non-equivalent sites produces satisfactory agreement with the description of the spectra of other compounds with the $ThMn_{12}$-type structure (see, for example, refs. 13–15). It should be noted that, in the pseudo-ternary alloys, a distribution of hyperfine fields, resulting from the varying number of Al atoms in the close vicinity of the Mössbauer atom, is taken into account by approximating the experimental spectra for different linewidths of the external and internal lines, *i.e.* $\Gamma_{1-6} > \Gamma_{2-5} > \Gamma_{3-4}$. Moreover, in the fitting procedure only these variants have been considered in which the surfaces of the sextet lines are close to the ratios 3:2:1:1:2:3 (excluding the aligned samples). The results are presented in Fig. 1 by solid lines. It follows from this figure that an increasing substitution of Al for Fe results in a change in the intensity of the sextet lines corresponding to different Fe sublattices. The intensity of the sextet corresponding to the 8i sublattice decreases quickly, reaching almost zero for $x \geq 2.5$. It is obviously connected with the increasing occupation of this sublattice by Al atoms. The increase in the number of Al atoms hardly changes the intensity of the sextet corresponding to the 8j positions, whereas the strong absorption in the range between the first and second lines of the spectrum demonstrates the considerable increase in the Fe contribution to the 8f sites in alloys with $x \geq 2.5$.

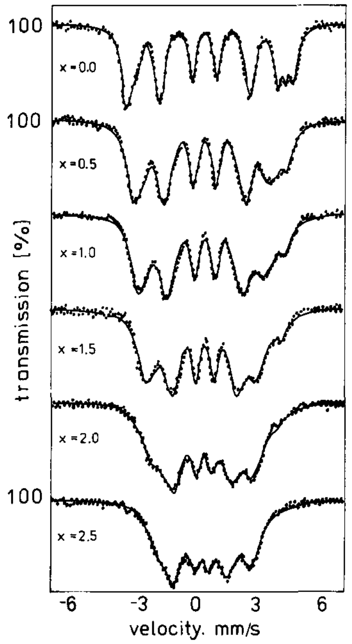
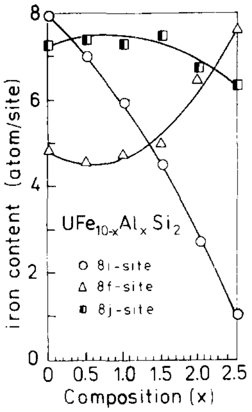


Fig. 1. ^{57}Fe Mössbauer spectra of $UFe_{10-x}Al_xSi_2$ system at 14 K for $0 \leqslant x \leqslant 2.5$.

In Fig. 2, one can see the distribution of the Fe atoms among various crystallographic positions, depending on the Al concentration x. The selective occupation of the 8i positions by the Al atoms is reflected also in a variation of the lattice parameters with x. It is easy to observe that the change of the parameter a, which is directly related to the 8i site occupation, is more pronounced than that of parameter c (see Fig. 1 in ref. 10). The linear relationship between lattice parameter a and the number of the Al atoms in the 8i sites, as shown in Fig. 3, also supports the above conclusion.

The Mössbauer and X-ray examination allow the mean number of nn Fe atoms and the average Fe–Fe separation to be determined for each type of crystallographic site. The results are presented in Figs. 4(a) and 4(b).



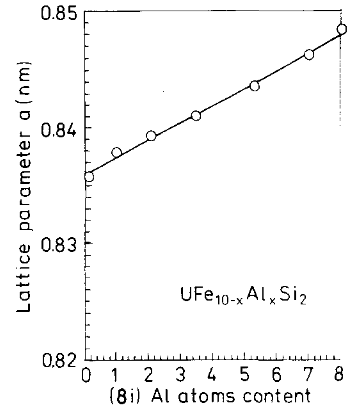


Fig. 2. Fe content in the 8i, 8j and 8f sites *vs.* Al concentration x.

Fig. 3. Lattice parameter a *vs.* Al content in 8i sites.

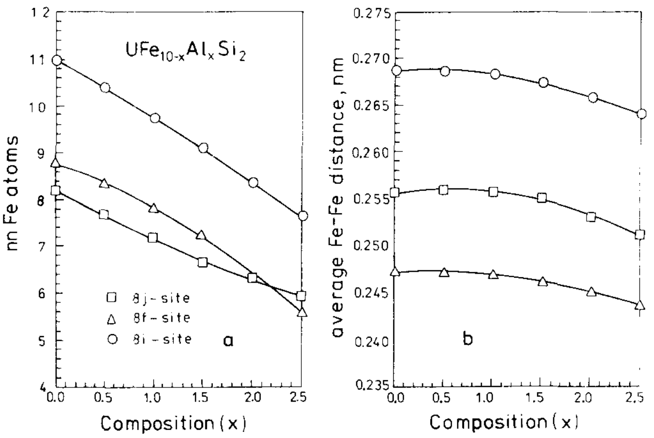


Fig. 4. (a) Number of the nearest neighbour (nn) Fe atoms *vs.* Al concentration x in different crystallographic positions. (b) Average Fe–Fe distance *vs.* Al concentration x.

Except for the geometrical effects resulting from the replacement of the Fe atoms by the Al atoms, strong decreases in the hyperfine field can be observed for each type of crystallographic sites. This is apparently connected to a decrease in the number of nn Fe atoms as well as to a decrease in the average Fe–Fe separation. Although the substitution of Fe by Al results in a pronounced increase in both lattice parameters ($\Delta a = 0.0133$ nm and $\Delta c = 0.0091$ nm), a decrease in the number of Fe atoms with the largest interatomic distance (d_{8i-8i}, d_{8i-8j} and d_{8i-8f}) results in a decrease in the average d_{Fe-Fe} separation for the atoms located in all the crystallographic sites. This phenomenon is followed by a strong diminution of the average hyperfine field (see Fig. 5(b)), and the same holds for the average magnetic moment localized on the Fe atom. This last value is calculated using a conversion factor of $14.5T/\mu_B$ [16]. For comparison, the results of the magnetization measurements [10] are presented in the form of circles.

The difference between the values can be attributed most probably to the contribution of the U sublattice.

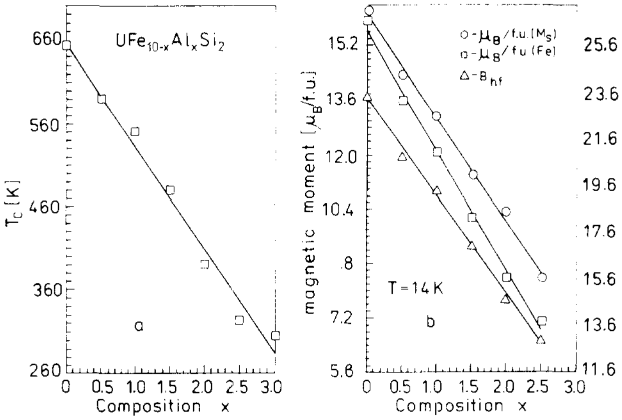


Fig. 5. (a) Curie temperature *vs.* Al concentration x (Fig. 2 in ref. 10). (b) Magnetic moment determined from magnetization measurements (○) (see Fig. 2. in ref. 10) and calculated from Mössbauer experiment (□) and average hyperfine field (△) at 14 K.

It can be seen that the diminution of the magnetic moment as the concentration of Al increases, as observed in the present investigations, is faster than that determined in the magnetization measurements. The U magnetic moment increases from 0.5 μ_B for $x = 0$ to 1.4 μ_B for $x = 2.5$. This rise can be explained by a decrease in 5f–3d hybridization with decreasing Fe content. In the UFe_xAl_{12-x} system without Si, the concentration dependence of μ_s has a minimum at $x = 4$ where nearly all the Fe atoms occupy the 8f positions and are ordered antiferromagnetically. The minimum value 1.6 μ_B can be attributed to the U magnetic moment. The results obtained in the present paper are in good agreement with this value, especially taking into account that the Fe concentration and, consequently, the 5f–3d hybridization in UFe_4Al_8 are lower.

The observed change in the U magnetic moment points to some error in the calculation of the magnetic anisotropy contributions made in ref. 10 under the assumption of an unchanged state of U upon Fe–Al substitution. The actual situation is more complicated.

The other reason for the difference increasing could be a change in the hyperfine interaction parameter, although firm conclusions can be derived only from more advanced experiments (*e.g.* neutron diffraction on single-crystal samples).

In Fig. 5(a) the Curie temperatures *vs.* x are plotted (see Fig. 2 in ref. 10). With increasing x, the Curie temperature decreases strongly but linearly. This decrease correlates with the decrease in the magnetic moments.

It can be seen from Fig. 4(a) that for $x = 2$ the quantities of nn Fe for positions 8j and 8f are equal. For this concentration, the average Fe–Fe distance for the 8f sites is 0.245 nm, which can be considered as a critical distance. The further increase of x, therefore, could be a reason for a change in the magnetic interactions from ferromagnetic to antiferromagnetic (in the 8f sites). The coexistence of the ferromagnetic ordering in the 8i sublattice with the antiferromagnetic interactions mentioned above can set up clusters in a spin-glass state. The distribution of hyperfine fields in these clusters, as well as fluctuations of the magnetization direction, can lead to Mössbauer spectra having a relaxation line in the central part of the spectrum. In Fig. 6, the spectra of the alloys with $x=2.5$ and 3.0 are described fairly well after introducing an additional central relaxation line which is presented separately by a solid line.

This part of the discussion is rather tentative but the strong decrease in the number of Fe atoms in the 8i positions, the equal numbers of nn Fe atoms for 8j and 8f sites and the decrease in the Fe–Fe separation below a critical value for $x \geq 2$ are most probably the reasons for the change in the type of magnetocrystalline anisotropy (easy axis to easy plane) reported in ref. 10 for this composition.

In Fig. 7, we show the spectra obtained at 14 and 295 K for aligned samples with $x=1$. The close similarity of both spectra excludes the possibility of a temperature-driven spin reorientation transformation, at least between 14 and 295 K for this composition.

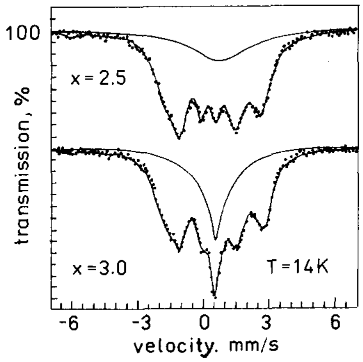


Fig. 6. ^{57}Fe Mössbauer spectra of alloys with $x=2.5$ and 3.0 at 14 K. Central solid line represents relaxation line.

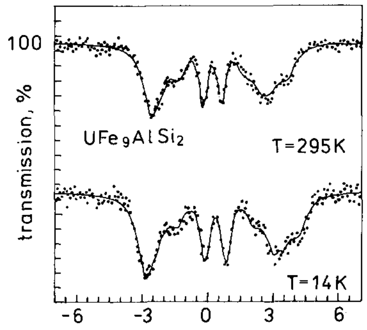


Fig. 7. ^{57}Fe Mössbauer spectra of aligned sample of UFe_9AlSi_2 at 14 and 295 K.

4. Conclusions

Our results of Mössbauer examination of the $UFe_{10-x}Al_xSi_2$ system show that the Al atoms mainly occupy the 8i sites. This distribution of the Al atoms results in a diminution of the average Fe–Fe distance for all the crystallographic sites, as well as in a weakening of the ferromagnetic exchange interactions. The last phenomenon causes a decrease in the Fe hyperfine fields, and the corresponding Fe moment decrease leads to a diminution of the Curie temperature. For compounds with $x \geq 2$, the average separation between the Fe atoms in the 8f sites is comparable with the critical separation (and even less). This fact together with the decrease in the number of Fe atoms located at 8i sites seem to be the reasons for the concentration-driven spin reorientation transitions (change of magnetocrystalline anisotropy type) observed in the magnetization examination [10].

The difference between the magnetic moments determined from magnetization measurements and those calculated from hyperfine field values is a good reason to believe that there is a contribution of the U sublattice to the magnetic ordering. This contribution should be of a ferromagnetic type, as is reported also in ref. 11.

Finally, it should be stressed that the above discussion makes sense only when one assumes a prevailing effect of the geometrical factors. This assumption seems to be justified, because trivalent Fe is replaced by trivalent Al. However, this assumption is not necessarily true and a change in the band structure could be the real reason for the observed behaviour.

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