Magnetic properties of U1-xThxAs and UAs1-xSex compounds

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Magnetic properties of $U_{1-x}Th_xAs$ and $UAs_{1-x}Se_x$ compounds

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Résumé. — La variation thermique de la susceptibilité magnétique des composés $U_{1-x}Th_xAs$ et $UAs_{1-x}Se_x$ a été obtenue par une méthode d'inductance mutuelle. Le diagramme de phase magnétique de ces composés a été déterminé en champ nul. Au-dessus de la température d'ordre, des anomalies, des pics et des sauts, ont été observés pour les deux séries de composés. Des expériences par diffraction neutronique s'avèrent nécessaires pour déterminer si ces anomalies sont dues à des changements de phase magnétique. Pour les composés $U_{1-x}Th_xAs$, comme pour les composés $UAs_{1-x}Se_x$, le thorium et le sélénium apportent des électrons de conduction supplémentaires. L'analogie dans le comportement magnétique de ces deux séries de composés nous permet de conclure que les électrons de conduction jouent un rôle important dans leurs propriétés magnétiques.

Abstract. — The thermal variation of the magnetic susceptibility of $U_{1-x}Th_xAs$ and $UAs_{1-x}Se_x$ compounds has been investigated by a mutual inductance technique. The magnetic phase diagram of these two compounds has been determined in zero field. Anomalies as peaks or jumps have been evidenced in the thermal variation of the magnetic susceptibility for both series of compounds, above the ordering temperature. Neutron diffraction experiments are necessary to know if these anomalies are associated with changes in the magnetic structures. For $U_{1-x}Th_xAs$, as for $UAs_{1-x}Se_x$ compounds, additional conduction electrons are provided by thorium and selenium. The similarities between the magnetic behaviour of these compounds show that the conduction electrons play a fundamental rôle in their magnetic properties.

1. Introduction.

The uranium monopnictides with the NaCl structure exhibit complex and original magnetic properties [1-4]. Strong anisotropic exchange interactions have been observed leading to an Ising-like behaviour and complex magnetic phase diagrams. Several authors propose that the proximity of the 5f level near the Fermi energy is important in explaining this unusual behaviour [4, 5]. These properties could be attributed to a strong p-f hybridization due to the existence of holes in the valence band [4, 5]. However this hypothesis is not yet confirmed. The determination of the magnetic phase diagrams of these compounds is an important step towards their understanding.

In this paper, we will concentrate on the diluted and substituted UAs compounds, $U_{1-x}Th_xAs$ and $UAs_{1-x}Se_x$. In these two series of compounds, additional conduction electrons are respectively provided by thorium and selenium and consequently important changes in the p-f mixing are expected. If the p-f hybridization plays any fundamental rôle in the magnetic behaviour of UAs, then we could hope to see changes when the number of U and As atoms decreases. A consequence of the substitution of U by Th atoms is a decrease in the exchange interactions due to the dilution of the U atoms and an expansion of the lattice [6]. However we do not know if the valency of U atoms is independent of the Th and Se concentrations whose variations would have effects on the magnetic properties of these solid solutions.

The magnetic phase diagrams in high field as well as the magnetic structures in zero field have been already investigated in several compounds [7-13] and some of these results are reported in this paper. However, the main purpose of this work is to determine the thermal variation of the magnetic susceptibility of $U_{1-x}Th_xAs$ and some $UAs_{1-x}Se_x$ compounds using an a.c. low field, in order to obtain accurately the phase diagram in zero field and to compare the magnetic behaviour of these two series of compounds. Firstly we describe the experimental set up specially adapted to perform these measurements, then we report and discuss the results.

2. Experimental device.

The purpose of the experiment is to investigate at low temperatures the thermal variation of the magnetic susceptibility of samples using a low a.c. field (about 10 Oe). The measurements of the susceptibility were performed using a compensated mutual inductance coil method (Fig. 1) and the low temperatures were obtained with a closed cycle He system (displex CS-202 of air products corporation) as shown in (Fig. 2). The sample is set up at one end of a cylindrical holder, 60 mm long and 4 mm in diameter in order to place the sample in the middle of the upper mutual inductance coil. The other end of the holder is in thermal contact with the cold head of the refrigerating system which can be cooled down to 10 K. The holder is made of about 1 100 isolated copper wires stuck together with an epoxy resin to both reduce the eddy current effects on the signal and to allow the heat transfer between the refrigerating head and the sample. A platinum resistance thermometer calibrated at ice melting and nitrogen boiling points is located just below the sample. The assembly is placed in the tail of a glass cryostat and maintained under a primary vacuum. The tail is introduced inside the pick-up coils in such a way that the sample lies at the center of the upper mutual coil. The calibration constant of the pick-up coils being sensitive to thermal gradients, the coils were kept at constant temperature, inside a cryostat containing liquid nitrogen. Variation of the sample temperature between 30 K and room temperature is obtained by heating the head of the refrigerator and the temperature is stabilized by a thermal regulation. This device gives a signal stability better than 10^{-3}.

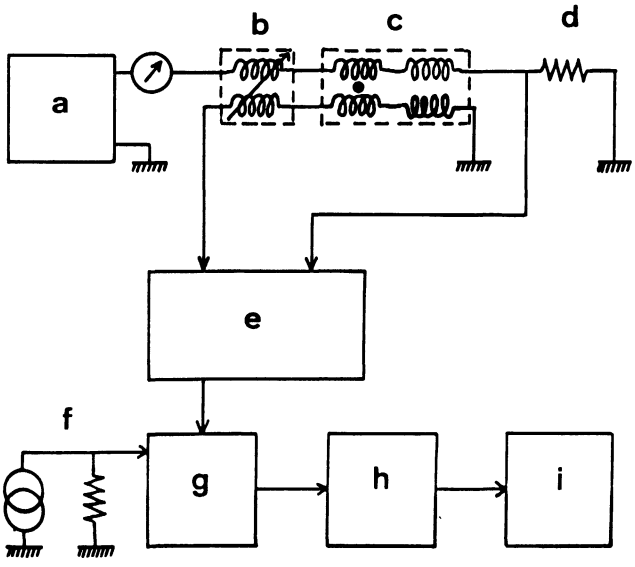

Fig. 1. — Electrical block diagram of the experiment : a) Sine generator, b) Mutual standard inductance coils, c) Pick-up mutual coils and sample, d) Standard resistance, e) Two phase/vector lock in amplifier, f) Platine resistance thermometer, g) Data acquisition system, h) Micro-computer, i) Results output device.

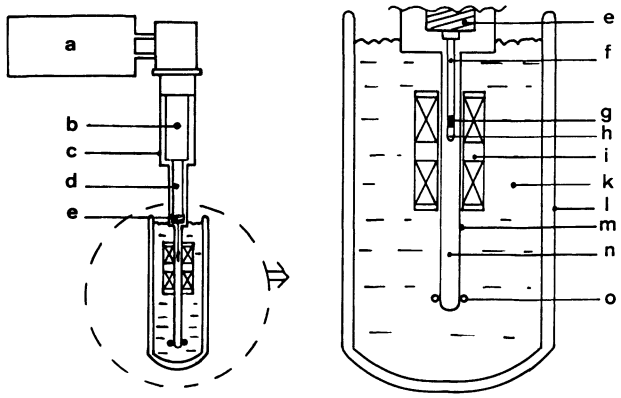

Fig. 2. — Diagram showing the experimental set-up : a) Helium compressor for the closed-cycle refrigerator, b) Closed-cycle refrigerating system, c) Glass cryostat, d) Refrigerated head, e) Heating wire, f) Cu holder, g) Sample, h) Pt resistance thermometer, i) Pick-up coils, k) Liquid nitrogen bath, l) Dewar, m) Glass cryostat tail, n) Primary vacuum, o) Tail stop for pick-up coils when the reference signal is measured.

The pick-up coils were made with isolated copper wires wound on a body in talc mixed with epoxy resin. Wires of 0.2 and 0.1 mm in diameter were used for the primary and the secondary circuits of the coils, respectively. The pick-up coils were placed in series with a calibrated mutual inductance that permits a shift in the pick-up signal to increase significantly the performance of the measurement device (Fig. 1). The current in the primary coil is supplied by a low frequency generator and maintained at a constant value of 60 mA with a stability better than 10^{-3} during the experiment. The value of the frequency is 80 c/s. The primary and the secondary signals of the coils are transfered to a two phase vector lock-in amplifier of Princeton Applied Research Corporation which measures the total impedance $Z = Z' - jZ''$, and particularly the real part Z' which is proportional to the magnetic susceptibility of the sample. In fact, Z' is not only due to the sample susceptibility but also to its surroundings, and more particularly to the holder. The contributions of the holder, of the glass cryostat, and of the thermometer have been found nearly constant and negligible with respect to the sample signal. At low temperatures the eddy-currents increase progressively but are not strong enough to affect significantly the feature of the curve. In order to limit the effect of the signal shift during the experiment and to get reproductible measurements, the value of the reference signal was subtracted from the measured signal associated with Z'. The reference signals were determined when the pick-up coil was placed at the bottom of the tail cryostat. To obtain this last position, the coil can move along the cryostat down to the end of the tail (Fig. 2). Then,

to return to the measurement position, the coil is moved up, until the signal reaches an extremum value, and then is fixed. With this method, the reference signal can be determined several times and measured at the beginning and at the end of the experiment which permits the detection of any signal shift during a run. The values of the magnetic susceptibilities are then deduced from the difference between the two signals, multiplied by the calibration constant. With this device a sensitivity of 10^{-7} uem has been obtained. A data acquisition system regularly records the temperature and mutual coil signals and the results are obtained directly after data processing.

3. Results.

In order to check and calibrate our experimental device, the thermal variation of the magnetic susceptibility of a UAs single crystal was first investigated. The $\langle 001 \rangle$ direction was oriented along the axis of the pick-up coils. Our results shown in figure 3 are comparable with the results obtained by Troć and Lam [14].

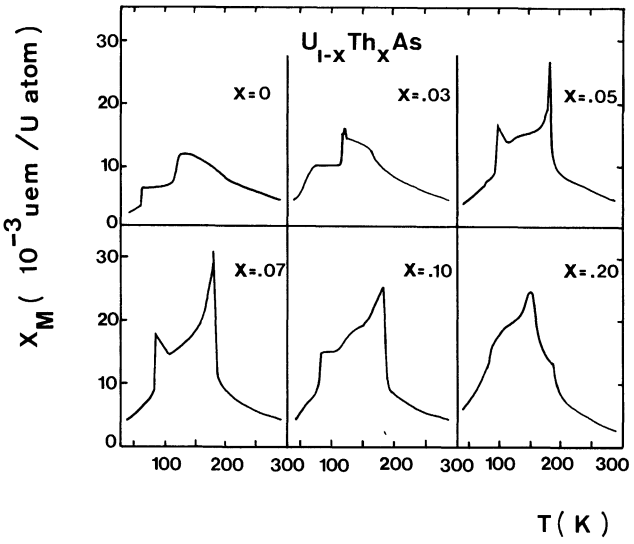

Fig. 3. — Thermal variation of the magnetic susceptibility of $U_{1-x}Th_xAs$ compounds determined by the mutual inductance technique as described in the text, for $x < 0.20$.

Except for the value of the jump of the lowest transition temperature, which is greater in our case, the results over the whole range can be compared with a relative accuracy of better than 10 %. Taking account of this analysis the results of Troć and Lam have been used to calibrate our experiment. No extra-anomalies appear (Fig. 3) which could be due to the surrounding of the sample (cryostat, sample holder, body of the coil, etc.). This last remark has its importance in the following.

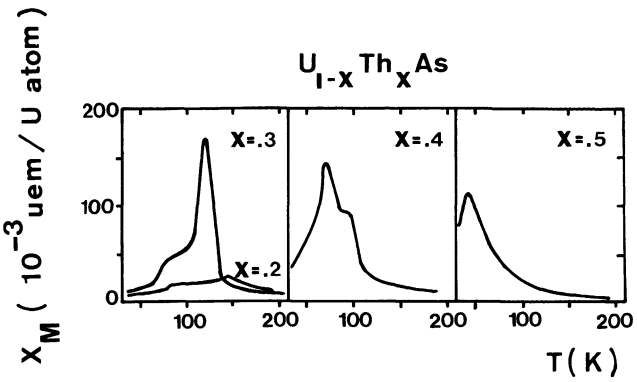

Fig. 4. — Thermal variation of the magnetic susceptibility of $U_{1-x}Th_xAs$ compounds determined by the mutual inductance technique for $x > 0.20$. For $x = 0.30$, the susceptibility curve $x = 0.20$ (lower curve) has been reported for comparison.

3.1 $U_{1-x}Th_xAs$ SOLID SOLUTIONS. — The thermal variations of the magnetic susceptibility of the $U_{1-x}Th_xAs$ solid solutions can be separated into two kinds of behaviour depending on the concentration of thorium. For $x < 0.3$ (Fig. 3) the values of the

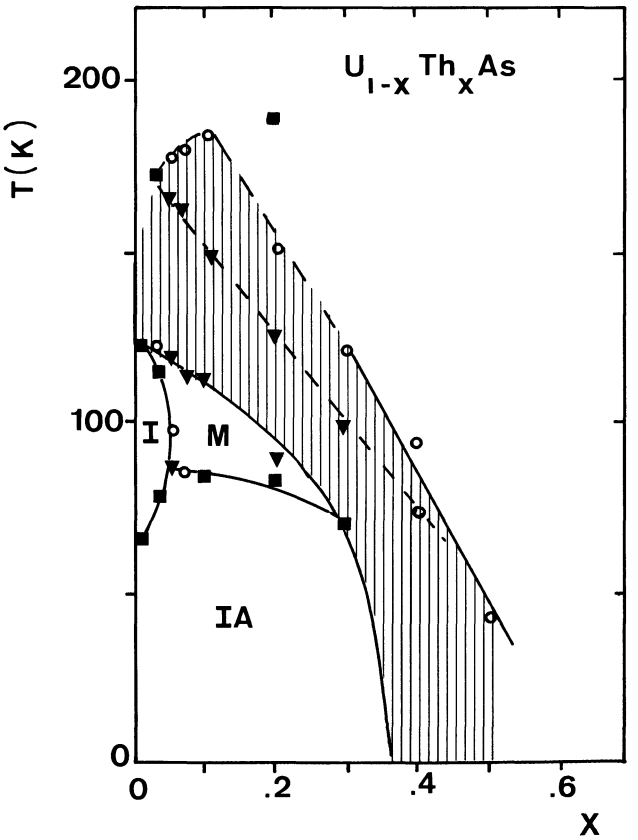

Fig. 5. — Magnetic phase diagram of $U_{1-x}Th_xAs$ compounds in a temperature (T) *versus* concentration (x) plot in zero field. The hatched part has been pointed out in this work and is discussed in the text. Phase I is an antiferromagnetic phase of type I, IA is an antiferromagnetic phase of type IA, M is a modulated phase [7-10].

magnetic susceptibilities are comparable in amplitude with that of UAs, whereas for $x \geqslant 0.3$ these values are greater (Fig. 4). The progressive substitution of uranium by thorium atoms leads to anomalies in the magnetic susceptibility (Fig. 3 and Fig. 4). The low temperature anomalies are characteristic of phase transitions as reported on the non-hatched part of the T, x plot (Fig. 5). These phases were previously examined by bulk magnetic measurements up to $x = 0.1$ [7, 8, 10], and by neutron diffraction up to $x = 0.3$ [9]. Our results are consistent with these at least in the non-hatched part of our phase diagram for $x < 0.3$. As seen in figure 5, for increasing temperature, and large uranium concentrations two antiferromagnetic phases of type IA and I appear successively, whereas for $x > 0.05$ the phase IA is followed by a modulated phase and the phase I has disappeared.

The hatched part of the phase diagram (Fig. 5) corresponds to the new results deduced from the experiments reported here (Fig. 3 and Fig. 4). Our results are not sufficient to be sure of the existence of magnetic ordered phases in this region and for this reason, this part of the phase diagram has been hatched. However, anomalies in the magnetic susceptibility show that, in this phase diagram region, the sample exhibits peculiar behaviour which needs special investigation.

3.2 $U_{1-x}Th_xAs$ FOR $x < 0.3$. — The substitution of uranium by thorium atoms gives rise to additional peaks and jumps in the thermal variation of the magnetic susceptibility in contrast with UAs (Fig. 3). Some anomalies occur above the ordering temperatures given in the literature at least for $x < 0.3$. The peaks appear even for a rather small amount of thorium (Fig. 3) and their amplitude varies significantly when the concentration of thorium increases (Fig. 3). At the same time, whereas one peak disappears, another one grows or disappears at a different temperature. The existence of peaks above the ordering temperature is confirmed by the observation of an inflexion point in the thermal variation of the magnetization at constant field. This behaviour may be due to a short range order above the ordering temperature or to an incommensurate magnetic phase. In these two cases, careful neutron diffraction experiments in this temperature range are needed to clarify this question.

However, if we cannot explain the origin of these peaks above the ordering temperature, it is important to notice that they appear as soon as uranium is replaced by thorium atoms. Therefore, this effect is probably due mainly to the insertion of thorium atoms and in this sense, the contribution of the additional conduction electrons might be certainly very important, as we will see in the following analyses.

3.3 $U_{1-x}Th_xAs$ FOR $x \geqslant 0.3$. — The second series of compounds with $x \geqslant 0.3$ exhibits a large peak of the susceptibility, ten times bigger than those observed for the series $x < 0.3$ as shown figure 4, in which are respectively reported the results for $x = 0.2$ and $x = 0.3$. The increase of the thorium amount gives rise to a decrease in the exchange interactions as observed in figure 4. Indeed, the magnitude and the temperature of the peaks decrease when x increases. Most of this behaviour is confirmed by the bulk magnetic measurements in high field at 80 kOe [7], as shown in figure 6, for different concentrations of thorium. For the high concentration of thorium $x > 0.3$, the magnetization magnitude becomes clearly greater than the susceptibility in low field. These last results may have their origin in the character change of exchange forces as we have already proposed in a previous communication [10]. As shown on figure 7, this change seems to be proved by the

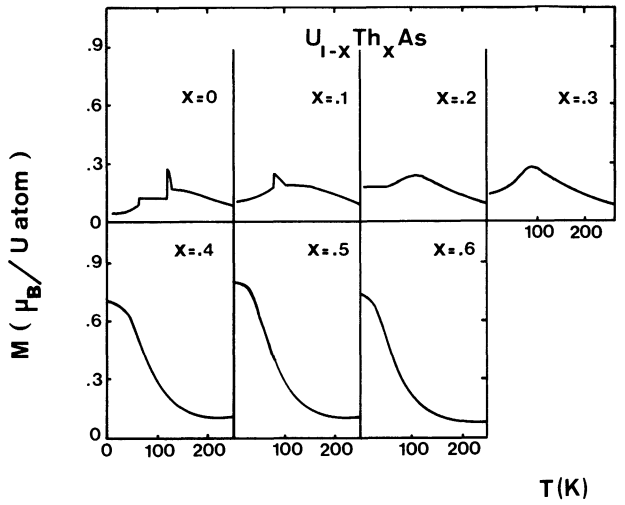

Fig. 6. — Thermal variation of the magnetization of $U_{1-x}Th_xAs$ single crystals at constant magnetic field (80 kOe) applied along a $\langle 001 \rangle$ axis for different values of x.

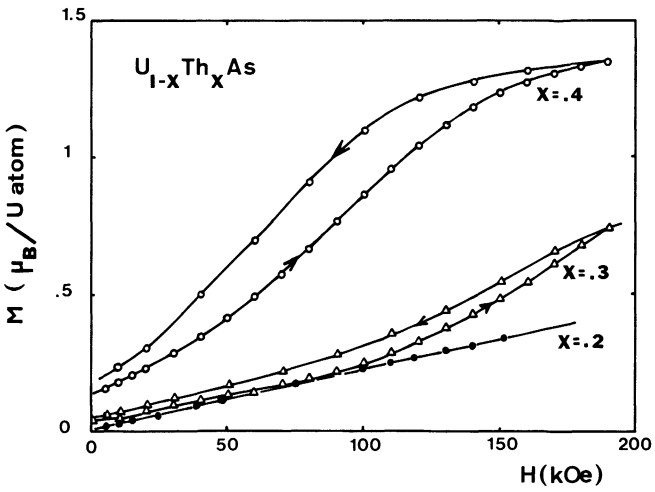

Fig. 7. — Magnetization *versus* field of three $U_{1-x}Th_xAs$ compounds at 4.2 K, with field applied along a $\langle 001 \rangle$ direction.

magnetization curves of some $U_{1-x}Th_xAs$ compounds (x = 0.2, 0.3 and 0.4) determined at 4.2 K and in high field. Such a behaviour has been already observed for the $UAs_{1-x}Se_x$ solid solution [11]. For these last compounds, ferrimagnetic and ferromagnetic phases are proposed for large concentrations of Se.

See figure 9 and next paragraph.

3.4 $UAs_{1-x}Se_x$ SOLID SOLUTIONS. — In order to corroborate this special behaviour of the $U_{1-x}Th_xAs$ solid solutions, similar experiments were investigated on $UAs_{1-x}Se_x$ compounds. The thermal variation of the magnetic susceptibility of some $UAs_{1-x}Se_x$ compounds is reported on figure 8. These results can be compared with the magnetic phase diagram determined in high field [11] (Fig. 9). Good agreement between the results is observed except for the hatched part of the phase diagram which is suggested by the measurements here. As previously found in the $U_{1-x}Th_xAs$ solid solutions, this specific region of the phase diagram is situated above the ordering temperature.

The effect of magnetic field on magnetization in this temperature and concentration range is presented

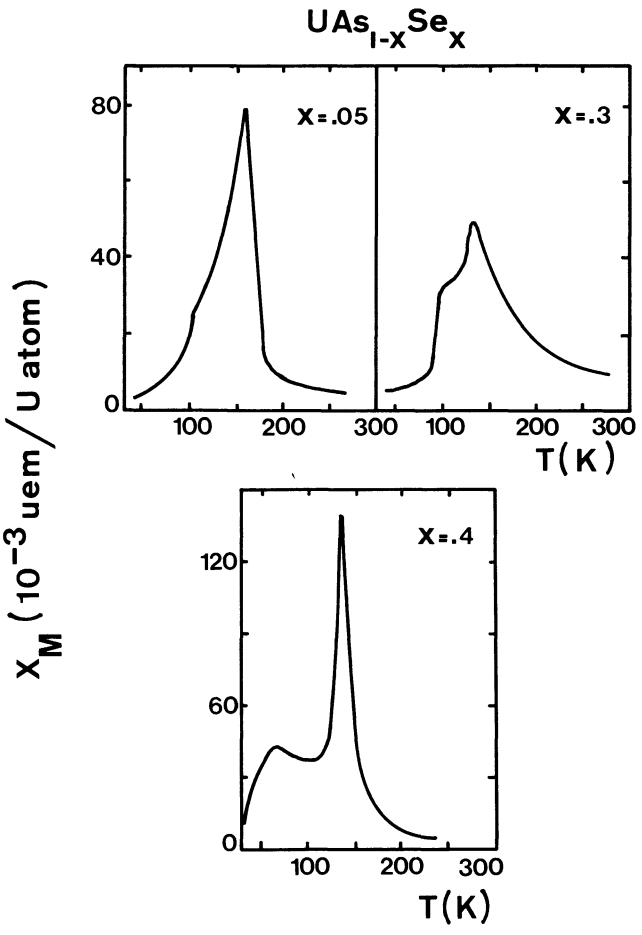

Fig. 8. — Thermal variation of the magnetic susceptibility of $UAs_{1-x}Se_x$ compounds determined by the mutual inductance technique; note the change of scale on graph x = 0.40.

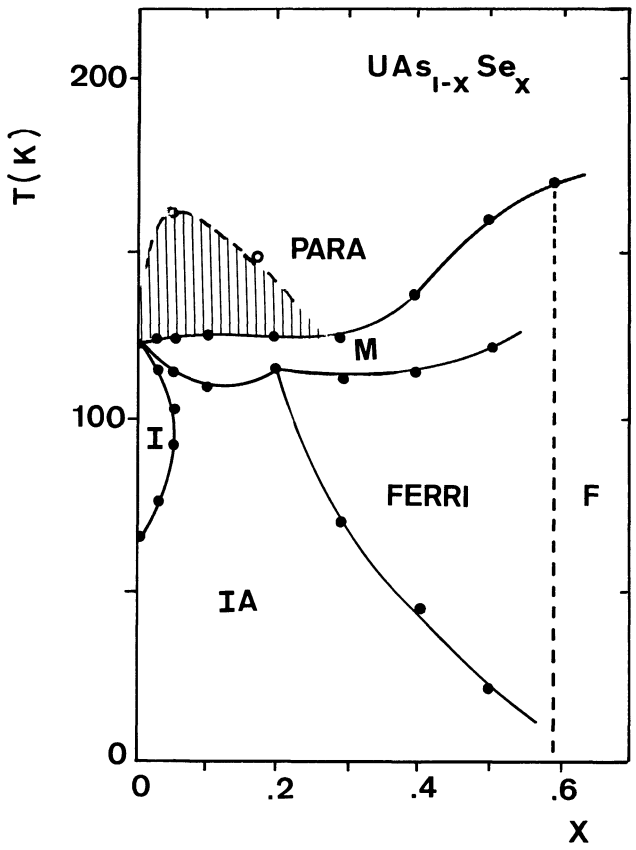

Fig. 9. — Magnetic phase diagram of $UAs_{1-x}Se_x$ compounds in a temperature (T) *versus* concentration (x) plot. The non-hatched part of this diagram arising from reference [11] is in good agreement with our results reported figure 8; phase I is the type I antiferromagnetism; IA is the type IA antiferromagnetism; M is a modulated phase; FERRI is a ferrimagnetism phase; F is the ferromagnetic phase; PARA is the paramagnetic phase. The hatched part of the diagram has been suggested by this work and is discussed in the text.

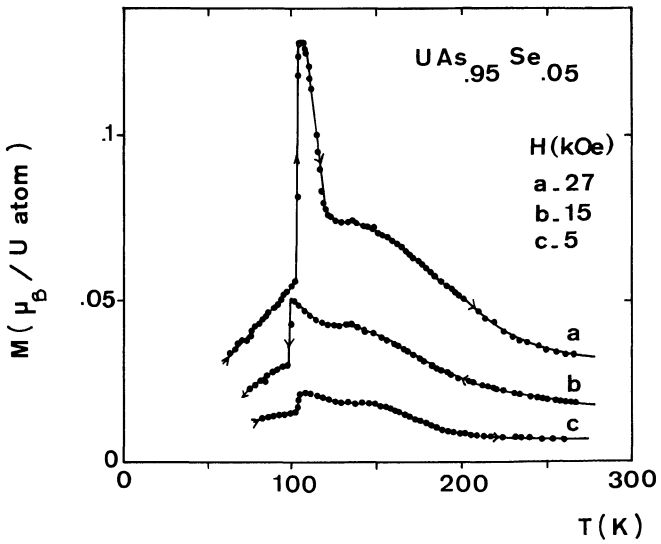

Fig. 10. — Thermal variations of the magnetization of a $UAs_{0.95}Se_{0.05}$ single crystal in high magnetic field applied along a $\langle 001 \rangle$ axis. H = 27 kOe (a), H = 15 kOe (b), H = 5 kOe (c).

on figure 10 and figure 11 for different field values. These last results were obtained by bulk magnetization measurements performed on a $UAs_{0.95}Se_{0.05}$ single crystal with field applied along a $\langle 001 \rangle$ axis. The peak observed in the thermal variation of the susceptibility and above the ordering temperature (Fig. 8) corresponds to the maximum evidenced on the magnetization curve c in low field (Fig. 11) and to the inflexion point for larger fields (Fig. 10 and Fig. 11).

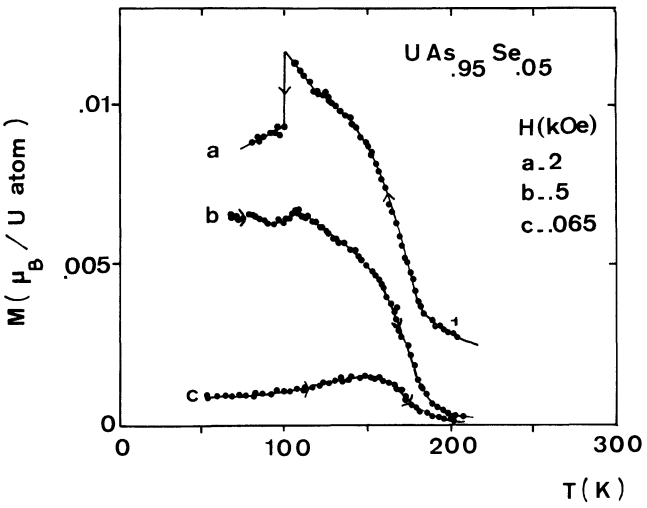

Fig. 11. — Thermal variations of the magnetization of a $UAs_{0.95}Se_{0.05}$ single crystal in low magnetic field applied along a $\langle 001 \rangle$ axis. $H = 2$ kOe (a), $H = 0.5$ kOe (b), $H = 0.065$ kOe (c).

4. Discussion.

Interesting results arise from the previous analyses. For the two series of compounds, peaks are observed above the ordering temperature. For large concentrations of thorium or selenium the magnitude of the susceptibility increases is as observed by other authors for the $UAs_{1-x}Se_x$ series [12-13], and a large peak is observed which has been associated with a change of magnetic ordering [11]. A similar behaviour has been observed in UAs-US solid solutions [15-18]. When the concentration of S increases the (T, x) magnetic phase diagram of $UAs_{1-x}S_x$ compounds [17] exhibits at all temperatures a successive phase change just as when the quantity of Th or Se increases respectively in $U_{1-x}Th_xAs$ and $UAs_{1-x}Se_x$ compounds. The hatched part of the phase diagram evidenced by this work does not signify that new magnetic phases exist above the ordering temperature. However the thermal variation of the magnetic susceptibility shows clearly a specific behaviour in this region.

In $UAs_{1-x}S_x$ solid solutions the increase in S provides additional conduction electrons as Th and Se do in the previously studied compounds. The magnetic phase changes are quite similar in these three series of compounds, whereas in every case conduction electrons are added, it is now very clear that these additional conduction electrons play a fundamental rôle in the magnetic properties of these solid solutions. Although these results could provide an excellent argument for a strong p-f hybridization in these compounds and in particular in UAs [19], additional experiments are needed, in particular to know if the valency of the uranium atoms is conserved in these solid solutions.

Careful neutron experiments would be very valuable to illuminate further the magnetic phase diagram of these compounds and the physical phenomena observed above the ordering temperature for large concentrations of U or As.

Acknowledgments.

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References

[1] Rossat-Mignod, J., Burlet, P., Quezel, S., Vogt, O., *Physica* **102B** (1980) 237.

[2] Lander, G. H., *Actinides in Perspective*, Ed. Norman Edelstein, (Pergamon Press) 1982, p. 107.

[3] Rossat-Mignod, J., Burlet, P., Quezel, S., Vogt, O. and Bartholin, H., *Crystalline Electrical Field Effects in f. Electron Magnetism*, Ed. Guertin, R. P., Suski, W. and Zolnierek, Z. (Plenum Press, N. Y.) 1982, p. 501.

[4] Rossat-Mignod, J., Burlet, P., Quezel, S., Effantin, J. M., Vogt, O., Bartholin, H., VII International Conference on Solid Compounds of Transition Elements (Ed. Masson) *Ann. Chim. Fr.* **7** (1982) 471.

[5] Takegahara, K., Takahashi, H., Yanase, A. and Kasuya, T., *J. Phys. C* **14** (1981) 737.

[6] Ferro, R., Atomic Energy Review Special Issue N. 5 (IAEA, Vienna) (1975) 143.

[7] Vogt, O. and Bartholin, H., *J. Mag. Mag. Mat.* **15-18** (1980) 531.

[8] Vogt, O., *Physica* **102B** (1980) 206.

[9] Fisher, P., Schefer, J. and Vogt, O., *Physica* **102B** (1980) 192.

[10] Bartholin, H., Vogt, O., Breandon, C. and Tchapoutian, R., Communication at Actinides 1981 Asolimar Conference, Grounds Pacific Grove, California (1981).

[11] Vogt, O. and Bartholin, H., *J. Mag. Mag. Mat.* **29** (1982) 291.

[12] LECIEJEWICZ, J., TROĆ, R., MURASIK, A. and PALEWSKI, T., *Phys. Status Solidi* (b) **48** (1971) 445.

[13] OBOLENSKI, M. and TROĆ, R., Proc. 2nd Int. Conf. Electr. Structure Actinides, Wrocław (1976) 397.

[14] TROĆ, R. and LAM, D. J., *Phys. Status Solidi* (b) **65** (1974) 317.

[15] TRZEBIATOWSKI, W. and PALEWSKI, T., *Bull. Acad. Pol. Sci., Ser. Sci. Chem.* **19** (1971) 83.

[16] LECIEJEWICZ, J., MURASIK, A., TROĆ, R. and PALEWSKI, T., *Phys. Status Solidi* (b) **46** (1971) 391.

[17] LANDER, G. H., MUELLER, M. H. and REDDY, J. F., *Phys. Rev. B* **6** (1972) 1880.

[18] SUSKI, W., PALEWSKI, T. and MYDLARZ, T., *Int. J. Magnetism* **4** (1973) 305.

[19] BARTHOLIN, H., EFFANTIN, J. M., BURLET, P., ROSSAT-MIGNOD, J. and VOGT, O., *Crystalline Electric Field Effects in f. Electron Magnetism*, Ed. Guertin, R. P., Suski, W. and Zołnierek, Z. (Plenum Press, N. Y.) 1982, p. 393.