

Magnetic phase transitions in the $\text{UFe}_{1-x}\text{Co}_x\text{Al}$ system

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We present the results of x-ray-powder diffraction, magnetic susceptibility, magnetization, electrical resistivity, and Mössbauer effect measurements performed on the $\text{UFe}_{1-x}\text{Co}_x\text{Al}$ system. The lattice parameters determined for the system show a sharp maximum for $a(x)$ and minimum for $c(x)$ approximately for $x \approx 0.3$. From the point of view of magnetic properties this system appears to have two main concentration regions: (a) $0 \leq x < 0.5$ and (b) $0.5 \leq x \leq 1.0$. The phases falling into the first region do not show a long-range magnetic ordering, while in the second region they become ferromagnetic with the maximum values of the Curie temperature and spontaneous magnetic moment at $x \approx 0.8$. The ferromagnetic properties of the alloys at $B=0$ T with $0.5 \leq x \leq 0.98$ are also confirmed by the Mössbauer effect experiment. Furthermore, we compare the magnetic behavior of $\text{UFe}_{1-x}\text{Co}_x\text{Al}$ with that of the analogous $\text{UFe}_{1-x}\text{Ni}_x\text{Al}$. We find that the maximum ferromagnetic response appears in both systems by introduction to them of approximately 0.8 or 1 more electron, i.e., for the $x=0.8$ and 0.5 compositions, respectively. Moreover, we discuss the complex magnetic properties of pure U-Co-Al in more details and some view on its ground state is given. [S0163-1829(96)07446-2]

I. INTRODUCTION

In the UTM series, where T is a transition metal and M is a p -electron metalloid, the ground state of uranium atoms strongly depends on its T partner. It has been demonstrated that the gradual filling of the nd states with electrons causes the magnetic properties of the UTM compounds to develop from an itinerantlike paramagnetic behavior (U-Fe-Al, U-Co-Si, U-Co-Ge), through spin fluctuations (URuM), and itinerant ferromagnetism (URhM) to magnetic local-moment ordering (UNiM, UPdM, and UPtM).^{1,2} Therefore, the magnetic behavior of the UTM compounds depends not only on the U-U spacing, but also correlates strongly with the degree of the $5f$ - nd hybridization, which decreases rapidly with electron filling of the nd state.

In order to obtain a better understanding of the influence of $5f$ - nd hybridization effects on the physical properties of UTM series, we have earlier investigated the pseudoternary $\text{UFe}_{1-x}\text{Ni}_x\text{Al}$ system by means of magnetic and Mössbauer effect measurements.³ The results have shown a rapid increase in the correlation between the uranium magnetic moments near $x \approx 0.35$, and the occurrence of ferromagnetism for compositions with larger values of x , which in turn disappears at $x \approx 0.75$. The maximum values of both the Curie temperature and spontaneous magnetic moment of uranium have been found at $x \approx 0.5$. Finally, the alloys with $x \geq 0.9$ develop an antiferromagnetic ordering as U-Ni-Al does.

In this paper, we present experimental results obtained for the $\text{UFe}_{1-x}\text{Co}_x\text{Al}$ system and compare its magnetic behavior with that of the analogous $\text{UFe}_{1-x}\text{Ni}_x\text{Al}$ one. It appears that the main difference is that Co introduces one electron to the system, whereas Ni can introduce two. Both end compounds U-Fe-Al and U-Co-Al (low-temperature phases) are isostructural and crystallize in the hexagonal Ho-Ni-Al-type structure with similar lattice parameters ($a=6.672$ Å, $c=3.981$ Å, and $a=6.682$ Å and $c=3.974$ Å, for U-Fe-Al and U-Co-Al, respectively).^{4,5} In spite of this fact, their magnetic properties are quite different. The well documented data on U-Fe-Al (Refs. 1 and 6) indicate that this compound behaves as a weakly temperature-dependent paramagnet. On the other hand, U-Co-Al shows a very complex magnetic behavior. This stems from the fact that the observed broad maximum in the magnetization of U-Co-Al around $T \approx 16$ K and in low magnetic fields suggests the onset of an antiferromagnetic ordering below this temperature.⁷ In higher fields a metamagneticlike transition takes place. However, this transition does not proceed with a distinct jump in the magnetization as one could expect for a two sublattice magnetic system with a large anisotropy, but the magnetization rises gradually in some interval (0.5–1 T) of magnetic fields. The occurrence of the metamagnetic transition may be supported by the fact that this transition is accompanied by a magnetostriction effect.⁷ Furthermore, this effect cannot be explained by, e.g., the magnetization process of an uniaxial ferromagnet, be-

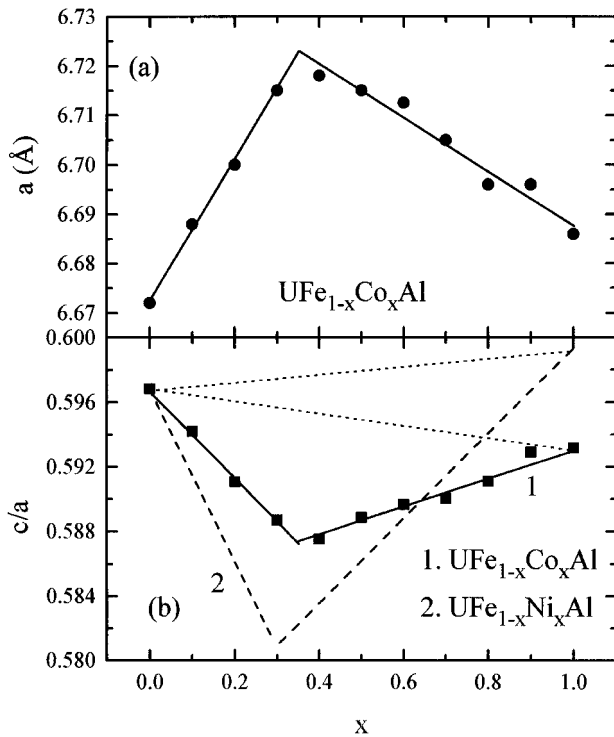


FIG. 1. (a) Lattice parameter a as a function of Co concentration x in the $\text{UFe}_{1-x}\text{Co}_x\text{Al}$ alloys. (b) The ratio c/a as a function of Co (experimental points) and Ni (dashed line) concentration x in the $\text{UFe}_{1-x}\text{Co}_x\text{Al}$ and $\text{UFe}_{1-x}\text{Ni}_x\text{Al}$ alloys, respectively. The dotted lines show the case of statistical occupancy of the sites by Fe and Co or Ni atoms. The solid lines are guides for the eye.

cause for the latter case the magnetostriction should be zero.⁷

It should be mentioned that the temperature dependence of both the electrical resistivity⁸ and specific heat⁹ show no anomaly around the magnetization maximum temperature. These results lead the authors of Refs. 8 and 9 to suggest that U-Co-Al is a paramagnet with strong spin fluctuation effects at low temperatures. The fact that the maximum in the magnetization mentioned above is very broad may explain to some extent why no anomaly is seen in the temperature dependences of electrical resistivity and heat capacity.

The magnetization on a single crystal of U-Co-Al shows this material to be strongly anisotropic with the easy magnetization direction along the c axis.⁹ In addition, the single-crystal magnetization curve taken in the easy magnetization direction exhibited a very large high-field susceptibility detected up to 35 T, being probably associated either with the presence of a large paramagnetic contribution into the ordered state or by a higher projection of the magnetic moment onto the c axis with increasing magnetic field strength (magnetic moment forms on angle with the c axis). The ratio between the calculated magnetic moments in 35 T, and that extrapolated to zero magnetic field was found to be larger than 2. Further detailed measurements with polarized neutron, performed on a single crystal of U-Co-Al in magnetic fields of 1.7 and 5 T, have demonstrated that this compound may be regarded as a band $5f$ metamagnet.^{10,11} This interpretation has been in line with the self-consistent linear muffin-tin orbital energy band calculations.^{12,13} Andreev¹⁴ investigated the range of homogeneity of U-Co-Al. The au-

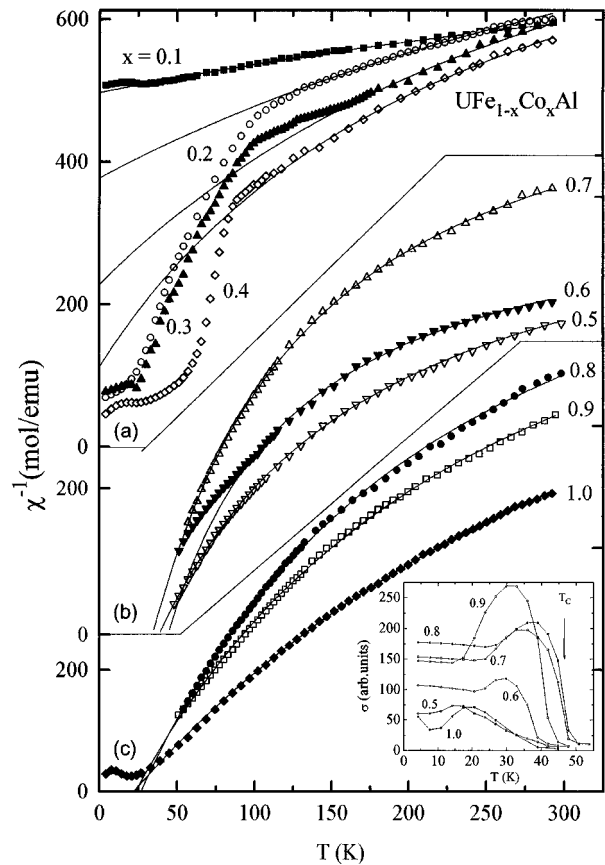


FIG. 2. Inverse magnetic susceptibility, χ^{-1} , as a function of temperature for the $\text{UFe}_{1-x}\text{Co}_x\text{Al}$ samples for: (a) $0.1 \leq x \leq 0.4$, (b) $0.5 \leq x \leq 0.7$, and (c) $0.8 \leq x \leq 1.0$. The solid lines are the fit of the experimental points by the modified Curie-Weiss law. The inset shows the magnetization at low temperatures. As an example, the arrow indicates the inflection point of the $\sigma(T)$ dependence for $x=0.8$, which was taken as the Curie temperature of this alloy.

thor found that the solid solution $\text{U}_x\text{Co}_{(3-x)/2}\text{Al}_{(3-x)/2}$ preserves the Fe_2P -type structure for $0.8 \leq x \leq 1.2$ (i.e., between $\text{U}_{0.8}\text{Co}_{1.1}\text{Al}_{1.1}$ and $\text{U}_{1.2}\text{Co}_{0.9}\text{Al}_{0.9}$) and the compositions with $x=0.8$ and 0.9 appeared to have a ferromagnetic component even in zero field. Recently, we have investigated U-Co-Al by means of neutron-diffraction measurements.¹⁵ We have suggested that our U-Co-Al compound may have the magnetic moments of uranium at low temperatures tilted by some angle from the c axis.¹⁵ The $\text{UFe}_{1-x}\text{Co}_x\text{Al}$ system seems therefore to be particularly suitable for the investigation, e.g., of the effect of the appearance of ferromagnetism in the system characterized by a fairly strong and anisotropic $5f$ - d electron hybridization.

II. EXPERIMENTAL DETAILS

The $\text{UFe}_{1-x}\text{Co}_x\text{Al}$ samples with $x=0.1$ – 0.9 , were synthesized by arc melting the constituent metals under a purified argon atmosphere. The samples were remelted several times and then annealed at 650°C for two weeks in vacuum sealed quartz ampoules. The homogeneity of samples was checked by electron microprobe analysis and x-ray diffraction.

dc-magnetic susceptibility measurements were carried out in the temperature range 4.2–300 K and in applied magnetic

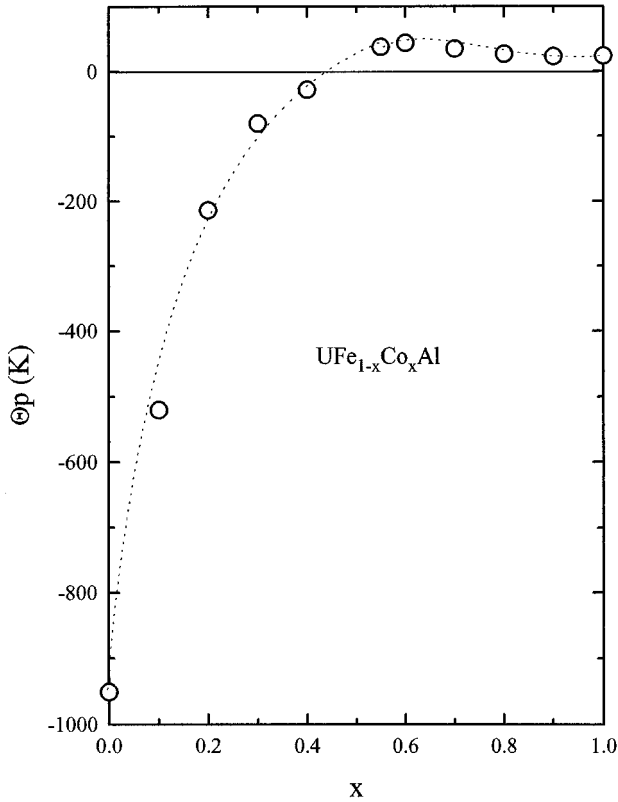


FIG. 3. Paramagnetic Curie temperature, Θ_p , as a function of Co concentration x .

fields up to 0.5 T, using a Faraday-type Cahn-RH electrobalance, while the ac-magnetic susceptibility was measured employing a Lakeshore susceptometer allowing the frequency range 33–666 Hz and applying external magnetic fields up to 5 mT. Magnetization measurements were performed at 4.2 K and in magnetic fields up to 4 T, using a moving sample magnetometer. The electrical resistivity has been measured only for U-Co-Al in the temperature range 1.2–300 K and in applied magnetic fields up to 1 T.

The ^{57}Fe Mössbauer studies were performed using a 57 Co/Rh(50 mCi) source and a conventional constant acceleration spectrometer Polon. The Mössbauer spectra were collected at 13 and 295 K. The velocity scale was calibrated using α -Fe absorber at room temperature.

III. RESULTS

A. X-ray diffraction

X-ray diffraction at room temperature showed that the $\text{UFe}_{1-x}\text{Co}_x\text{Al}$ samples were almost single phase having the hexagonal Ho-Ni-Al-type structure (space group $P62m$), i.e., the ordered version of the Fe_2P type. The unit cell contains uranium atoms in the (3g) sites with the aluminum atoms in the (3f) sites. The two remaining inequivalent positions (1b) and (2c) of this cell are occupied by the transition metals. The Fe_2P type and its ordered version have been discussed in details by Dwight *et al.*¹⁶ and by Hovesteydt *et al.*,¹⁷ who pointed out the same size of the unit cells for Fe_2P - and Ho-Ni-Al-type structure. In contrast, the Zr-Ni-Al-type structure, commonly used by many authors in the

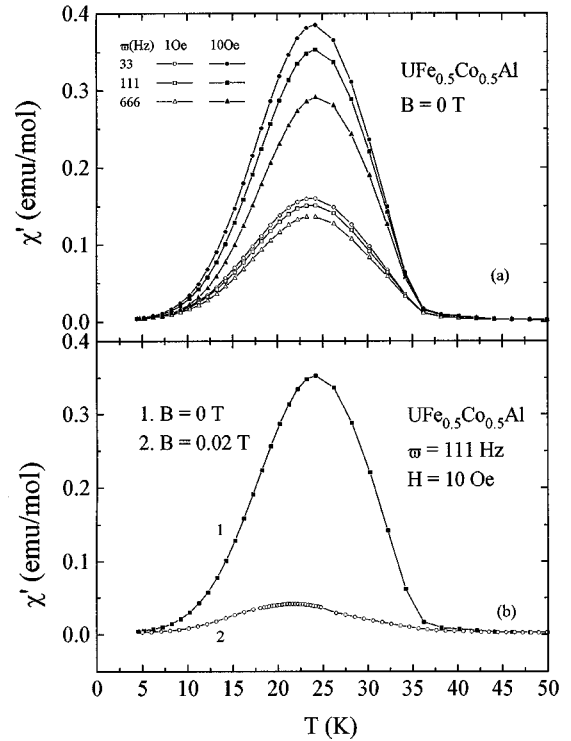


FIG. 4. Temperature dependence of the real part of the ac susceptibility, $\chi'(T)$, for $\text{UFe}_{0.5}\text{Co}_{0.5}\text{Al}$ (a) at frequencies of 33, 111, and 666 Hz and in magnetic ac fields of 1 Oe and 10 Oe and (b) at a frequency of 33 Hz and in an applied external magnetic field $B = 0$ and 0.02 T.

literature instead, has the unit cell volume of this structure doubled compared to the Fe_2P one.¹⁶

The variation in the lattice parameter a and in the ratio c/a of the $\text{UFe}_{1-x}\text{Co}_x\text{Al}$ samples upon composition x is shown in Fig. 1. From this figure it is clear that the Vegard law fails; the concentration dependence of both the parameters $a(x)$ and $c/a(x)$ show a strong anomaly at $x \approx 0.3$ –0.4. A similar compositional behavior of the lattice parameters, but even more manifested has already been observed by us in the $\text{UFe}_{1-x}\text{Ni}_x\text{Al}$ system.³ This unusual effect has been explained by the preferential occupation of Ni atoms at the (1b) site and hence implying a large increase in the valence electron density contribution at this site.¹⁸ This effect highly influences all the physical properties of these alloys. Here we are also dealing with the preferential occupation of Co atoms at the (1b) sites. However, the effect is not so distinctly manifested as in the case of Ni in the $\text{UFe}_{1-x}\text{Ni}_x\text{Al}$ system because of fewer electrons introduced by Co. It becomes clear if one compares in Fig. 1(b) the magnitude of anomaly effect in the lattice parameters near $x = 0.3$ for both systems in respect to the corresponding values determined by the Vegard law.

B. Magnetic susceptibility and magnetization

The temperature dependencies of the inverse susceptibility, $\chi^{-1}(T)$, for $\text{UFe}_{1-x}\text{Co}_x\text{Al}$ are collected in Fig. 2. As a general feature, all these phases in the concentration range $x = 0.1$ –0.4, do not show a long-range magnetic ordering down to the lowest temperature studied, namely, 4.2 K. Es-

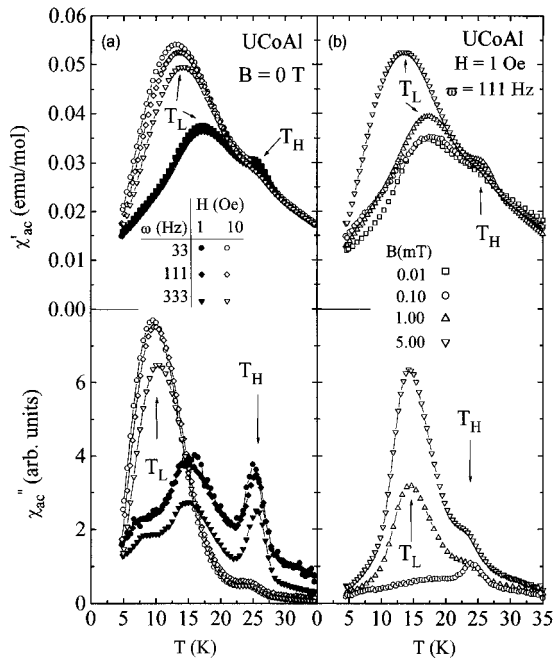


FIG. 5. Temperature dependence of the ac susceptibilities, $\chi'(T)$ and $\chi''(T)$, for the polycrystalline U-Co-Al sample measured with (a) different applied frequencies in zero external magnetic field, and (b) under different external magnetic fields and constant frequency.

pecially, the data for $\text{UFe}_{0.9}\text{Co}_{0.1}\text{Al}$ are quite similar to those of U-Fe-Al,⁶ i.e., the magnetic susceptibility is Pauli like being almost independent of temperature. For the $x=0.2-0.4$ samples, the $\chi^{-1}(T)$ dependencies show a curvature at high temperatures described by a modified Curie-Weiss law and a steady deviation from this law at low temperatures [Fig. 2(a)], due to the increasing presence of the correlation effect between the U moments. The pronounced S-shaped $\chi^{-1}(T)$ functions, well seen at low temperatures, resemble the behavior of some mictomagnetic phases below the so-called freezing temperature, T_f . However, the description of this kind of mictomagnetism in this concentration region requires a more detailed experimental study, which is not the purpose of this work. The effect of the presence in the samples of some ferromagnetic impurities should also be taken into account. However, we can exclude the potential impurities such as α -Fe and UFe_2 .¹⁹ It follows from the fact that the low-temperature end of a regular behavior of the inverse magnetic susceptibility (below about 100 K) [see Fig. 2(a)] is apparently lower than their ordering temperatures.

As mentioned above, in the temperature range 100–300 K, the $\chi^{-1}(T)$ functions could be analyzed by a modified Curie-Weiss behavior. The refined values of χ_0 are of the order 10^{-3} emu/mol and μ_{eff} changes from an unrealistic value of $4.2\mu_B$ for the $x=0.1$ sample (with a large negative Θ_p) to a more realistic value of $1.4\mu_B$ as x increases to 0.4. At the same time, all these alloys exhibit negative values of Θ_p , which become steadily reduced with increasing x content (see Fig. 3).

In Figs. 2(b) and 2(c), the magnetic susceptibility data are given for the Co-rich phases with $x \geq 0.5$. As seen from these figures, all the alloys in this concentration range exhibit a positive Θ_p value, indicating the possibility of the occur-

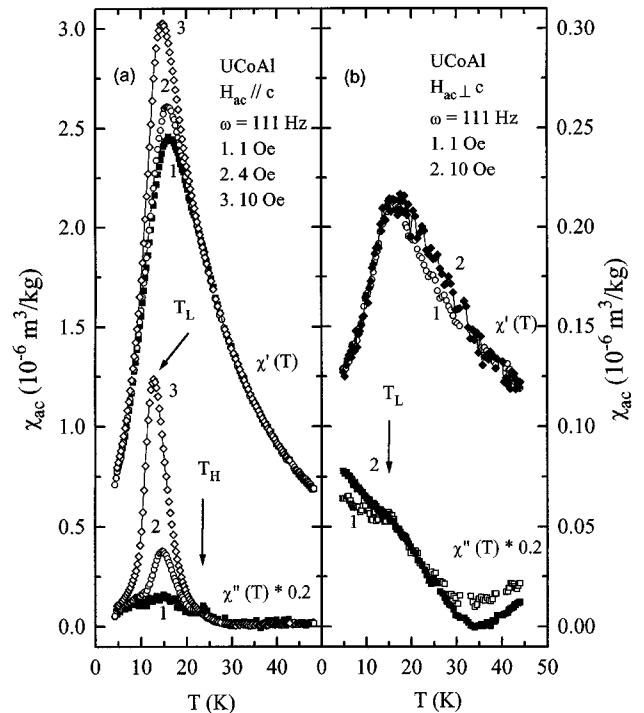


FIG. 6. Temperature dependence of the ac susceptibilities, $\chi'(T)$ and $\chi''(T)$, for the single crystalline U-Co-Al sample with H_{ac} being (a) parallel to the c axis and (b) perpendicular to the c axis.

rence of long-range ferromagnetic interactions between the uranium atoms. For U-Co-Al, the refined magnetic parameters ($\mu_{\text{eff}}=1.51\mu_B$, $\Theta_p=24.5$ K, and $\chi_0=0.8 \times 10^{-3}$ emu/mol) are comparable with those found for the c -axis susceptibility of U-Co-Al.¹⁴ However, the effective magnetic moment of uranium determined here is considerably lower than those reported for other similar ferromagnetic ternary 1:1:1 compounds, such as U-Rh-Al ($2.5\mu_B/\text{U}$)²⁰ and U-Ir-Sn ($2.3\mu_B/\text{U}$),²¹ but close to those reported for U-Co(Si,Ge).²²

At low temperatures, the magnetization curves, $\sigma(B)$, of the alloys with $x \geq 0.5$ show evidence for ferromagnetic order. Their Curie temperatures have been determined from the inflection point of the $\sigma(T)$ curves [inset of Fig. 2(c)]. Note that these curves do not have a typical shape for ferromagnetic materials. This unusual shape of $\sigma(T)$ with a maximum at higher temperatures may be caused by a strong anisotropy of these alloys in the ordered state. The Curie temperature, T_C , increases from about 25 K for $x=0.5$ to 47 K as the x value is increased to 0.8; then T_C is reduced with a further increasing x and for $x=0.95$ $T_C \approx 35$ K. The onset of the ferromagnetic state for $x > 0.45$ is also confirmed by the positive value of Θ_p for these compositions (Fig. 3).

The magnetization curves at 4.2 K for the alloys having x up to 0.4 become gradually enhanced and more curvilinear with increasing Co content. The moments calculated from the magnetization at 4.2 K and in a field $B=4$ T are, however, very small (i.e., $\mu \approx 0.03\mu_B$ for $x=0.4$). Otherwise, the magnetization curves at 4.2 K for the alloys with $x \geq 0.5$ become enhanced rapidly and are characterized by a hysteresis typical for ferromagnetic materials. For each sample, there is observed a steep increase in the magnetization at some critical field, B_{cr} . The B_{cr} value is related to the concentration x . For example, it is 0.25 T for $x=0.5$, and reaches

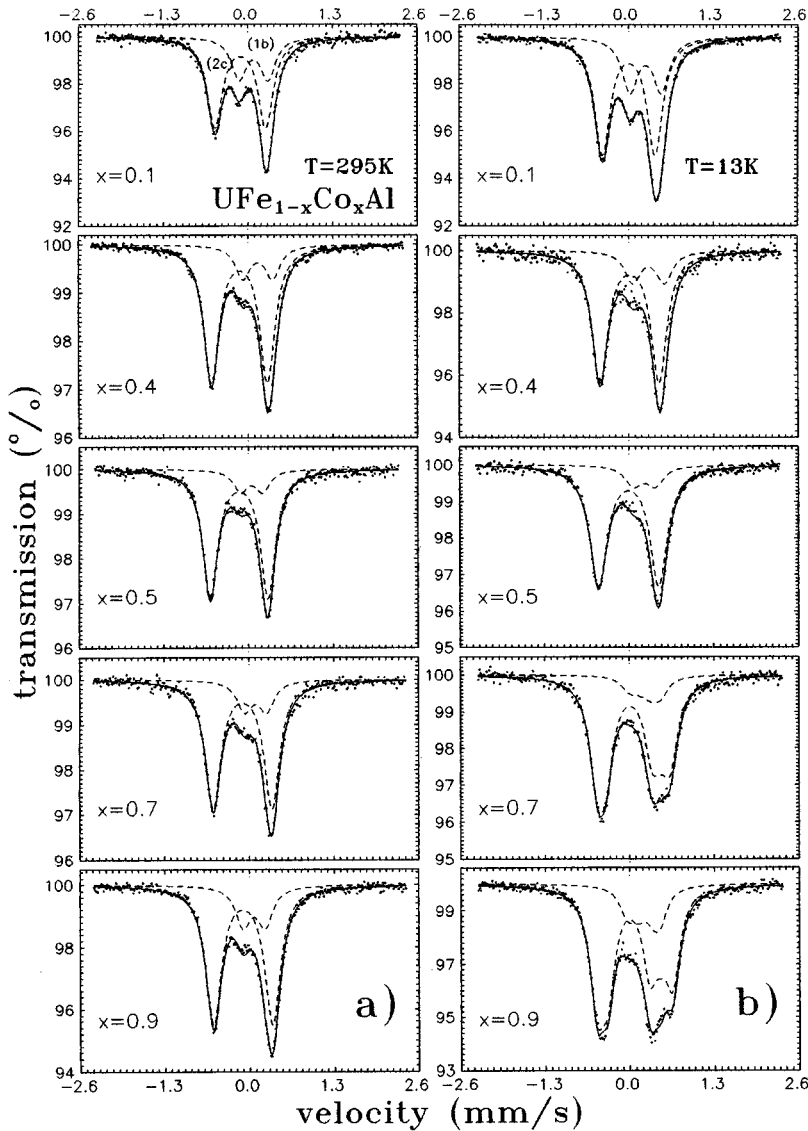


FIG. 7. Mössbauer spectra for the $\text{UFe}_{1-x}\text{Co}_x\text{Al}$ samples with $x=0.1, 0.4, 0.5, 0.7,$ and 0.9 : (a) at room temperature and (b) at 13 K.

a maximum value of 0.5 T for $x=0.7$, and then it decreases down to a value of 0.15 T for $x=0.95$. We interpret a sharp increase in the magnetization at B_{cr} by an inversion of the magnetic domains, as in the case of narrow Bloch-wall ferromagnetic materials. Furthermore, the magnetization of the $\text{UFe}_{1-x}\text{Co}_x\text{Al}$ ($x \geq 0.5$) samples reaches saturation relatively easy, but with some critical region at low magnetic fields. In general they exhibit a much simpler dependence of the magnetization on an applied magnetic field than that observed for the final composition U-Co-Al.^{7,9} It seems that the magnetic structure of the samples with $x=0.5-0.9$ is much simpler, i.e., the magnetic moments are probably parallel to the c axis, as has already been observed for the other studied UTM compounds with the hexagonal Fe_2P -type structure.^{23,24}

Consistent with the dc susceptibility, the zero-field ac-magnetic susceptibility measurements confirm ferromagnetic ordering at low temperatures for all compositions with $0.5 \leq x \leq 0.95$. As an example, Fig. 4 shows the real part of the ac susceptibility (χ') versus temperature for $\text{UFe}_{0.5}\text{Co}_{0.5}\text{Al}$. It is seen from this figure that the χ' component of the ac susceptibility exhibits a maximum located at the Curie temperature. This ferromagnetic phase transition is much clearer from the ac-susceptibility experiments per-

formed for three different frequencies and in ac fields $H=1$ Oe and 10 Oe [Fig. 4(a)]. The $\chi_{\text{ac}}(T)$ curves in both the ac fields show a maximum which shifts slightly towards higher temperatures as the ac-magnetic field increases. In the case of applied external magnetic fields, B , a shift of T_{max} towards lower temperatures and broadening of the $\chi'(T)$ maximum with a considerable reduction is well observed in Fig. 4(b). On the other hand, this figure also indicates that the temperature of the $\chi'(T)$ maximum is practically independent of frequency.

The same behavior of $\chi_{\text{ac}}(T)$ was observed for other compositions, such as $x=0.7, 0.8,$ and 0.9 , but not shown here. In each case, the $\chi'(T)$ maximum corresponds to T_C with values which agree well with those found from the $\sigma(T)$ curves.

The temperature dependence of the ac susceptibility of polycrystalline U-Co-Al measured for several frequencies 33, 111, and 666 Hz, and in ac fields $H=1$ and 10 Oe, is displayed in Fig. 5(a). In contrast to previous results,^{9,14} where the maximum in the dc susceptibility at $T=17$ K was reported to disappear in magnetic fields below 1 kOe, we can distinguish two anomalies in the $\chi_{\text{ac}}(T)$ curves at temperatures marked as T_L and T_H . The first low-temperature maximum occurs at $T_L=18$ K for $H=1$ Oe and $\bar{\omega}=333$ Hz and is

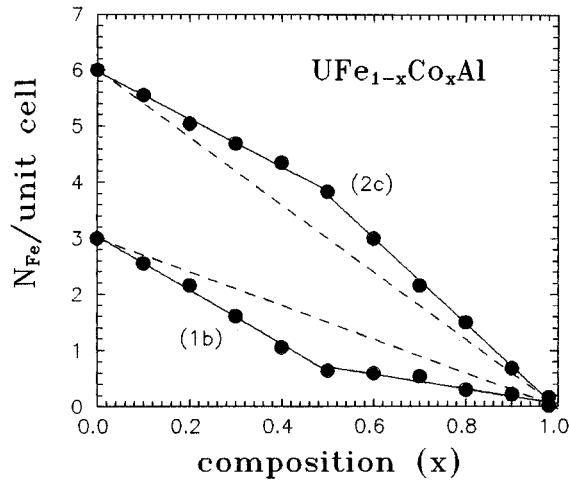


FIG. 8. The number of Fe atoms, $N_{Fe/unit\ cell}$, occupying the (2c) and (1b) sites as a function of Co concentration x . The size of experimental points represents approximately the error. The dashed line shows the case of statistical occupancy of the sites by Fe and Co atoms.

shifted down to 14 K for $H=10$ Oe and $\bar{\omega}=33$ Hz. The second, much smaller, maximum in $\chi_{ac}(T)$ occurs at about $T_H \approx 25$ K. In contrast to the low-temperature maximum, the position of T_H is almost independent of both the internal magnetic fields and frequencies. The transition at T_H is clearly seen in the temperature dependence of the imaginary susceptibility, $\chi''_{ac}(T)$ (bottom plot). At the same time, the maximum at T_L becomes enhanced on increasing both ac field, H , [Fig. 5(a)] and external field, B [Fig. 5(b)]. The distinct change in $\chi_{ac}(T)$ at T_L with $\bar{\omega}$, H and B observed in the measurements of polycrystalline U-Co-Al gives some indications of behavior characteristic for spin-glass systems.²⁵ This may be also in agreement with the domain effects of an anisotropic ferromagnetic material, as it was reported for the ferromagnetic compound U-Co-Ga, which exhibits a strong crystalline anisotropy.²⁶

In Fig. 6 we have presented the $\chi_{ac}(T)$ results obtained for a U-Co-Al single crystal applying various H from 1 to 10 Oe keeping $\bar{\omega}=111$ Hz. One sees that the ac susceptibility parallel to the c axis [Fig. 6(a)] shows the same magnetic response as the polycrystalline sample does. The χ' maximum at 15 K is enhanced in magnitude with increasing H and simultaneously the temperature of this maximum is decreased. This effect is seen considerably better in the temperature dependence of the imaginary part $\chi''_{ac}(T)$, but the anomaly at T_H is broadened with increasing ac-magnetic field. On the other hand, the ac-magnetic susceptibility measured perpendicular to the c axis [Fig. 6(b)] is very low, with the lack of any magnetic field effect. Nevertheless, the ac-susceptibility maximum at $T_L=15$ K is well detected in the $\chi'(T)$ curves.

C. Mössbauer effect

In our earlier study⁶ we have considered the Mössbauer spectra for U-Fe-Al, being in two crystallographic modifications: the low-temperature Ho-Ni-Al type and the high-temperature MgZn₂ type. The same situation occurs for the alloys containing 10% of Ni or Co. As was the case of

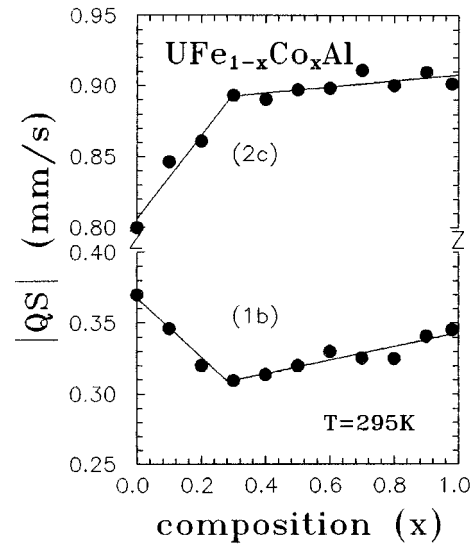


FIG. 9. The quadrupole splitting at 295 K for Fe at the (2c) and (1b) sites as a function of Co concentration x . The size of experimental points represents approximately the error. The lines drawn through the experimental points are guides for the eye.

$UFe_{0.9}Ni_{0.1}Al$ (Ref. 6) the room-temperature Mössbauer spectra of $UFe_{0.9}Co_{0.1}Al$ for these two crystallographic modifications correspond to the quadrupole doublets for the Fe atoms at the positions (1b) and (2c) with the average ratio 1:2 in the case of the Ho-Ni-Al-type structure and at the (2a) and (1b) positions with the ratio being 1:3 for the MgZn₂-type structure. The quadrupole splitting of the MgZn₂-type phase is considerably smaller than that for the Ho-Ni-Al-type phase. The alloys with $x>0.1$ are only of the Fe₂P type.

The Mössbauer spectra of some investigated samples with $x \geq 0.1$ at 13 and 295 K are presented in Fig. 7. As seen, the substitution Fe by Co atoms leads to the change in the intensity of lines corresponding to the Fe atoms at the (1b) and (2c) sites. Analyzing the areas under given subspectra obtained at 295 K, one can conclude that such a substitution up to the concentration $x=0.5$ takes place at Fe located at the (1b) sites, whereas for the samples with $x \geq 0.5$ only at the (2c) sites, as one can infer from Fig. 8. The dashed line in this figure gives the dependence on the number of Fe atoms in the hexagonal unit cell in the case of a random location of the Co atoms in the available crystallographic positions. A similar occupation of the (1b) sites, but by Ni in the $UFe_{1-x}Ni_xAl$ alloys, has already been analyzed in Ref. 3. For this system, the substitution process at these sites is practically finished at a Ni concentration not too higher than $x=0.3$, while in the case of the Co-based alloys this process lasts for almost the entire range of Co concentration, but with a different rate below and above $x=0.5$ (Fig. 8).

One of the possible reasons of the affinity to the (1b) site of Co and Ni atoms may be based on the geometrical sizes of these atoms. This site has a smaller Wigner-Seitz volume than the (2c) site does. Therefore, Fe atoms, having a larger radius ($R_{Fe}=1.26$ Å) in comparison to Co ($R_{Co}=1.25$ Å) and Ni ($R_{Ni}=1.24$ Å) atoms, is easily replaced in this position by a smaller atom, i.e., Co or Ni.

The crystal structure reconstruction is also revealed in the concentration dependence of the quadrupole splitting, $|QS|$,

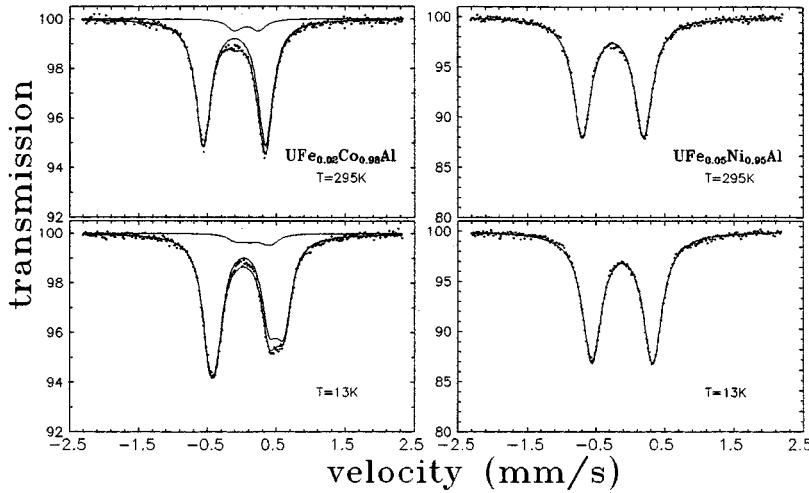


FIG. 10. Mössbauer spectra for the $\text{UFe}_{0.02}\text{Co}_{0.98}\text{Al}$ (left) and $\text{UFe}_{0.05}\text{Ni}_{0.95}\text{Al}$ (right) samples, respectively, at room temperature and 13 K.

of the Mössbauer lines, shown in Fig. 9. In this figure one sees a distinct break in this function at $x \approx 0.3$ for both the sites (1b) and (2c). This result corresponds almost ideally to their mutual ratio 1:2 in the unit cell. For the former site this break is less pronounced in absolute magnitude than for the latter site. Such a change in the $|QS|$ values is consistent with the change in the unit-cell parameters on composition (Fig. 1). Therefore, one can conclude that the change in the quadrupole interactions in these alloys is connected to a large extent with the lattice contribution to the electrical field gradient (EFG), because the Fe(Co) atoms for both sites do not have in their nearest surroundings other Fe(Co) atoms. In this context, it is probable that in the UAl systems, some shift in the position of the Al atoms in the middle region of concentrations ($x=0.3-0.7$) takes place, as was suggested in the $\text{UFe}_{1-x}\text{Ni}_x\text{Al}$ system.³

On the basis of Mössbauer spectra taken at 13 K, it is necessary to note that for all the compositions with $x \geq 0.5$, the transfer of magnetic hyperfine field, H_{hf} , on the nonmagnetic ^{57}Fe atoms was well detected with values depending on the concentration.

For the sake of comparison, we display in Fig. 10 the Mössbauer spectra for the ferromagnetic $\text{UFe}_{0.02}\text{Co}_{0.98}\text{Al}$ and

antiferromagnetic $\text{UFe}_{0.05}\text{Ni}_{0.95}\text{Al}$. The quadrupole doublets at room temperature for both kind of alloys are also shown in this figure. Following the above analysis it is clear that U-Co-Al shows the Mössbauer spectra indicating the presence of the transferred hyperfine field on ^{57}Fe , while for the antiferromagnet U-Ni-Al this field is averaged to zero. Although the magnetic structure of U-Ni-Al has not been well determined yet, the observed zero-magnetic splitting has to be the result of the compensation of the opposite arranged magnetic moments.

D. Electrical resistivity and magnetoresistivity

The electrical resistivity and magnetoresistivity have been measured only on the polycrystalline sample of U-Co-Al. The temperature dependence of the electrical resistivity, $\rho(T)$, taken in zero magnetic field for this compound does not show any indication of a magnetic phase transition down to 1.2 K (Fig. 11). Note that the absolute resistivity value of this material at 300 K is rather large ($650 \mu\Omega \text{ cm}$). At $T=1.2$ K, the residual resistivity is still high ($95 \mu\Omega \text{ cm}$). Nevertheless, the ratio $\rho(300)/\rho(4.2)=6.8$ may indicate a sufficiently high quality of this sample. The resistivity in the temperature

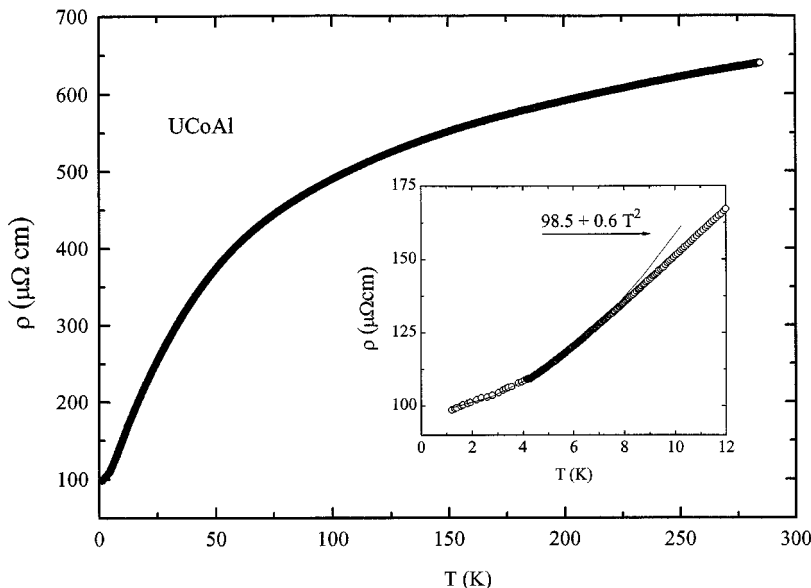


FIG. 11. Temperature dependence of the electrical resistivity of U-Co-Al. The solid line in the inset represents the $A T^2$ dependence of the resistivity.

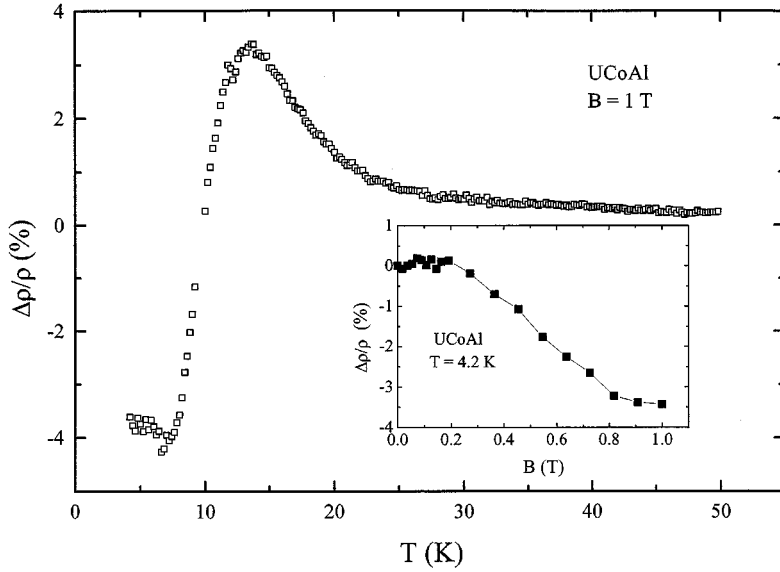


FIG. 12. Temperature dependence of the magnetoresistivity of U-Co-Al at $B=1$ T. Inset: the magnetoresistivity in magnetic fields up to 1 T measured at $T=4.2$ K.

range 1.2–8 K can be described by the relation $\rho(T) = 98.5 + 0.6T^2$. As the temperature is increased above 8 K, $\rho(T)$ first behaves linearly and then (above 50 K) shows the strong tendency to saturation. The similarity of this dependence to that exhibited by UAl_2 (Ref. 27) and other spin-fluctuators allows us to suggest that a significant influence of spin fluctuations on the magnetism of U-Co-Al should be taken into account as well.

The transverse magnetoresistivity data, $\Delta\rho(B)/\rho(B=0) = [\rho(B) - \rho(B=0)]/\rho(B=0)$, for U-Co-Al taken at 4.2 K and in magnetic fields up to 1 T are displayed in the inset of Fig. 12. A very small positive initial magnetoresistivity changes its sign at $B=0.2$ T, and then varies almost quadratically with increasing magnetic field strength, reaching about -3.5% at 1 T. Such a behavior of $\Delta\rho(B)/\rho(B=0)$ may be characteristic of a metamagnet, but as well as of spin-glass or short-range magnetic order. The above result is quite different from that found by Andreev for a U-Co-Al single crystal.¹⁴ This author reported the magnetoresistivity to be positive at this temperature up to $B=7.5$ T, i.e., a limit of his measurements.

In spite of a lack of any anomaly in $\rho(T)$, we do observe an anomaly in the temperature dependence of the magnetoresistivity measured in $B=1$ T (Fig. 12), which may be associated with a phase transition. This function is negative at 4.2 K, becomes zero at $T=10$ K, and exhibits a positive maximum around 14 K and then decreases to almost zero near 25 K. Usually such an anomaly occurs at a metamagnetic transition.²⁹

IV. DISCUSSION

In a previous paper²⁸ we proposed a preliminary magnetic phase diagram for the $\text{UFe}_{1-x}\text{Co}_x\text{Al}$ alloys, showing that the ferromagnetic state in these solid solutions is stable at $H=0$ Oe for compositions between $x=0.5$ and 1.0. In Fig. 13 we summarize the variation of the hyperfine field, H_{hf} , the Curie temperature, T_C , the spontaneous magnetic moment, μ_s , together with the previous results for μ_s .²⁸ All the values of these parameters go through a maximum at about the same concentration, namely at $x=0.8$.

It is clear that in a manner similar to the behavior of the $\text{UFe}_{1-x}\text{Ni}_x\text{Al}$ system, the substitution of Co for the Fe atoms in U-Fe-Al enhances strongly the magnetism, and in consequence leads to long-range magnetic ordering, with a critical concentration at $x \approx 0.5$. In view of the fact that the Co atoms have a smaller number of d electrons than Ni, the appearance of a spontaneous ferromagnetic moment in the $\text{UFe}_{1-x}\text{Co}_x\text{Al}$ system has to occur at a larger value of x , which is observed experimentally. This indicates the importance of the transfer of charge from the uranium atoms to the d band of a given transition metal atom. Hence, it becomes quite clear that for the system investigated here, in which Co has d bands less filled than in Ni, the maximum in T_C (and also in μ_s) must be reached for a higher concentration of x . However, it does not happen exactly at $x \approx 1$, as one might expect, compared

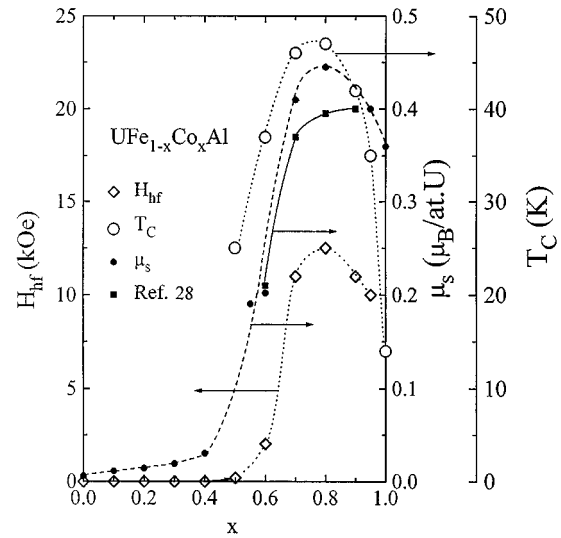


FIG. 13. Magnetic phase diagram for the $\text{UFe}_{1-x}\text{Co}_x\text{Al}$ system: T_C is the Curie temperature determined by the magnetization and ac susceptibility, μ_s is the spontaneous magnetic moment determined by magnetization at 4.2 K and in magnetic field of 4 T, and H_{hf} is the transferred hyperfine field, determined in zero magnetic field, all as a function of the Co concentration x . Full squares are the results of μ_s given in Ref. 28.

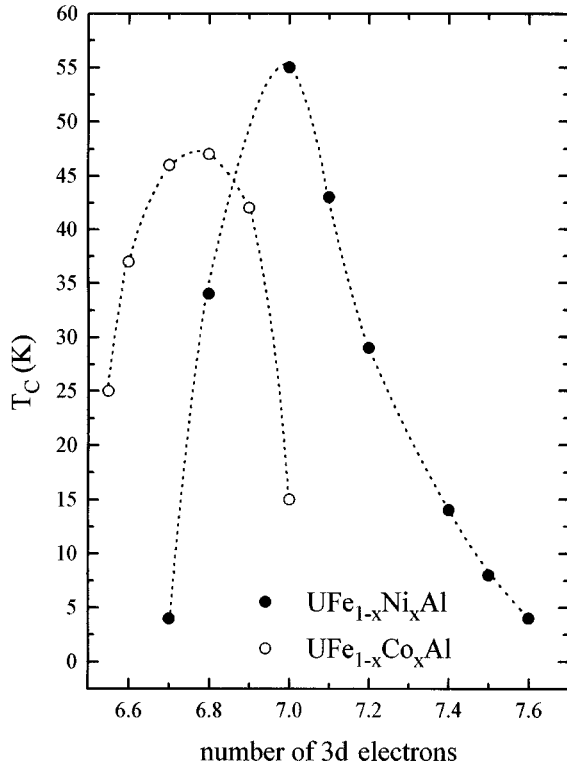


FIG. 14. Comparison of the ordering temperature vs the number of 3d electrons in the $\text{UFe}_{1-x}\text{Co}_x\text{Al}$ (open circles) and $\text{UFe}_{1-x}\text{Ni}_x\text{Al}$ (closed circles) systems.

to the system based on Ni (maximum at $x \approx 0.5$), but somewhat earlier, i.e., at $x = 0.8$, as shown in Fig. 14. Also the absolute values of T_C are lower than the corresponding values in the Ni system.

Besides the simple geometrical picture, the analysis of chemical bonding, carried out by us on the basis of theoretical calculations of the electron density distribution in the unit cell of U-Fe-Al, and made also for several $\text{UFe}_{1-x}\text{Ni}_x\text{Al}$ solid solutions, has pointed out that the substitution of the Fe atoms at the (1b) sites by the transition metal T , like Co or Ni, causes the polarization of the electron clouds from the (Al- T_2) plane towards the (U- T_1) plane, resulting in a mutual attraction of these planes.¹⁸ In consequence of this attraction, the lattice parameter c diminishes, while a increases. This tendency is most apparent for the Ni-substituted alloys,³ because this element introduces into the crystal structure about one electron more than Co does.

An analysis of the results of the magnetic data shows that the interaction between the U5f and Fe(Co) 3d electrons has a great influence on the magnetic properties of the $\text{UFe}_{1-x}\text{Co}_x\text{Al}$ alloys. There are two different factors that one can expect to play a role in the $T_C(\mu_s)$ vs x behavior. The first one is the number of 3d electrons in the system. If this number is too small, the 3d band becomes partially filled by a transfer of charge from the uranium atoms. In such a case, the 5f-3d hybridization is large and the band at E_F becomes broad and inhibits the formation of a stable magnetic moment. A similar effect has recently been observed by Andreev *et al.*³⁰ for polycrystalline $\text{UCo}_{0.9}\text{T}_{0.1}\text{Al}$ where $T = \text{Fe, Ru, Ni, and Pd}$. According to our results, the Fe and Ru substitution leads to an enhancement of ferromagnetism (T_C

and μ_s for both compositions are 45 K and $0.3\mu_B$, respectively), whereas the Ni and Pd substitution suppresses the magnetic moment. The second factor is the extent of the hybridization between the 5f and 3d states in the basal U- T_1 plane. The 3d-wave function for the Co atoms has a smaller spatial extent comparing to that of the Fe atoms. This may imply that the degree of U5f-Co3d hybridization is somewhat smaller than that of the U-Fe pair but higher than the U-Ni pair.

Analyzing Fig. 13, we can see that the system with $x < 0.5$ is likely to have no magnetic ground state (due to not having enough 3d electrons), whereas the phases with $x \geq 0.5$ become ferromagnetic due to the filling of the 3d bands with more electrons, and therefore the 5f-3d hybridization within the basal plane is rapidly reduced, but probably leaving the U5f-Al(sp) hybridization unchanged. However, the dependence of T_C and μ_s on x is not linear, and these effects mentioned above give rise to the observed increase in the T_C and μ_s values only up to $x \approx 0.8$. The quenching of the f moments in the alloys above this concentration is probably due to the increasing role of the Kondo spin compensation.³¹ This idea has been considered with the help of the Doniach diagram³² for interpreting the destabilization of ferromagnetism in the $\text{UFe}_{1-x}\text{Ni}_x\text{Al}$ system.³ Nevertheless, it is difficult to understand why such a mechanism could be responsible for the transition from the ferromagnetic to the antiferromagnetic state at the Ni concentration $x \approx 0.9$ in these alloys.³ Another explanation is probably that the hybridization between 5f and 3d electrons of the transition metal atoms at the (1b) sites (i.e., the interaction in the basal U- T_1 plane) yields the ferromagnetic-type interaction, whereas the U5f- and Al-sp hybridization (between planes) may lead to an antiferromagnetic-type of interaction. When the 5f-3d hybridization decreases, i.e., with increasing Co(Ni) concentration in the alloys, the ferromagnetic-type of fluctuations becomes comparable to the antiferromagnetic ones. Hence, T_C in the system is rapidly reduced and pure U-Co-Al can be characterized by complex ferro-antiferromagnetic interactions. In the presence of antiferromagnetic interactions, the triangular symmetry of uranium atoms in the basal plane intimately leads to the frustration of the moment components, at least the components in the basal U- T_1 plane. The latter would explain the small response on applied magnetic field within the basal plane found in the magnetization experiment on a U-Co-Al single crystal.^{7,9} On the other hand, the large contribution of the high-field susceptibility in the magnetization performed along the c axis (see Introduction) and a rapid rise of the susceptibility below 18 K, i.e., below the temperature of its broad maximum, measured also along this direction³³ may indicate that not all the U moments in U-Co-Al are ordered at low temperature. For example, this is the case of UNi_4B (Refs. 34 and 35) with a uranium atom arrangement similar to U-Co-Al. In the unit cell of the former compound one third of U moments is not ordered, while the remaining two third U moments have a vortex-type arrangement in the basal plane. This complex magnetic structure of UNi_4B leads to the similar $\chi(T)$ behavior below T_N as that mentioned above for the U-Co-Al case.

V. CONCLUSIONS

The $\text{UFe}_{1-x}\text{Ni}_x\text{Al}$ alloys have been investigated by different experimental techniques. Most of them confirm that in

the Co concentration range $x > 0.45$ the ferromagnetic state is onset with the maximum values of T_C , μ_s , and H_{hf} for $x \approx 0.8$. Further substitution weakens the ferromagnetic state probably due to a gradual increase of the antiferromagnetic interaction in a similar way as was the case of the $UFe_{1-x}Ni_xAl$ system. It therefore implies that finally in U-Co-Al both the ferromagnetic and antiferromagnetic interactions become equally important. In consequence this situation brings about a complex magnetic ground state in this compound, such as a strongly random magnetic ordering or spin-glass type of behavior. This picture is opposite to the prior view presented in the literature,¹⁰⁻¹³ that U-Co-Al is

the band metamagnet, i.e., is paramagnetic in zero magnetic field.

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- ¹V. Sechovský and L. Havela, in *Ferromagnetic Materials*, edited by E. P. Wohlfarth and K. H. J. Buschow (North-Holland, Amsterdam, 1988), Vol. 4, p. 309.
- ²R. Troć and V. H. Tran, *J. Magn. Magn. Mater.* **73**, 389 (1988).
- ³R. Troć, V. H. Tran, F. G. Vagizov, and H. Drulis, *Phys. Rev. B* **51**, 3003 (1995).
- ⁴D. J. Lam, J. B. Barby, Jr., J. W. Downey, and L. J. Norton, *J. Nucl. Mater.* **1**, 22 (1967).
- ⁵V. Ya. Markiv and P. I. Kripyakevich, *Kristallographica* **11**, 859 (1966).
- ⁶R. Troć, V. H. Tran, F. G. Vagizov, and H. Drulis, *J. Alloys Comp.* **200**, 37 (1993).
- ⁷A. V. Andreev, R. Z. Levitin, Yu. F. Popov, and R. Yu. Yumaguzhin, *Fiz. Tverd. Tela* **27**, 1902 (1985) [*Sov. Phys. Solid State* **27**, 1145 (1985)].
- ⁸V. Sechovský, L. Havela, L. Neuzil, A. V. Andreev, G. Hilschen, and C. Schmitzer, *J. Less-Common Met.* **121**, 169 (1986).
- ⁹V. Sechovský, L. Havela, F. R. de Boer, J. J. M. Franse, P. A. Veenhuizen, J. Sebek, J. Stehno, and A. V. Andreev, *Physica B* **142**, 283 (1986).
- ¹⁰M. Wulff, J. M. Fournier, A. Delapalme, B. Gillon, A. Sechovský, L. Havela, and A. V. Andreev, *Physica B* **163**, 331 (1990).
- ¹¹R. J. Papoular and A. Delapalme, *Phys. Rev. Lett.* **72**, 1486 (1994).
- ¹²O. Eriksson, B. Johansson, and M. S. S. Brooks, *J. Phys. C* **1**, 4005 (1989).
- ¹³T. Gasche, S. Auluck, M. S. S. Brooks, and B. Johansson, *J. Magn. Magn. Mater.* **104&107**, 37 (1992).
- ¹⁴A. V. Andreev, *Fiz. Met. Metalloved.* **5**, 77 (1990).
- ¹⁵V. H. Tran, R. Troć, F. Bourée, T. Roisnel, and G. André, *J. Magn. Magn. Mater.* **104-107**, 1377 (1995).
- ¹⁶A. E. Dwight, M. H. Mueller, R. A. Conner, Jr., J. W. Downey, and H. Knott, *Tran. Met. Soc. AIME* **242**, 2075 (1968).
- ¹⁷E. Hovestreydt, N. Engel, K. Klepp, B. Chabot, and E. Parthé, *J. Less-Common Met.* **85**, 247 (1982).
- ¹⁸I. M. Reznik, F. G. Vagizov, and R. Troć, *Phys. Rev. B* **51**, 3013 (1995).
- ¹⁹J. J. M. Franse, P. H. Frings, F. R. de Boer, and A. Menovsky, in *Physics of Solids Under High Pressure*, edited by J. S. Schilling and R. N. Shelton (North-Holland, Amsterdam, 1981), p. 181.
- ²⁰P. A. Veenhuizen, F. R. de Boer, A. A. Menovsky, V. Sechovský, and L. Havela, *J. Phys. (Paris), Colloq.* **49**, C 485 (1988).
- ²¹V. H. Tran and R. Troć, *J. Magn. Magn. Mater.* **102**, 74 (1991).
- ²²R. Troć and V. H. Tran, *J. Magn. Magn. Mater.* **73**, 389 (1988).
- ²³H. Fujii, H. Kawanaka, T. Takabatake, E. Sugiura, K. Sugiyama, and M. Data, *J. Magn. Magn. Mater.* **87**, 235 (1990).
- ²⁴H. Maletta, R. A. Robinson, A. C. Lawson, V. Sechovský, L. Havela, L. Jirman, M. Divis, E. Brück, F. R. de Boer, A. V. Andreev, K. H. J. Buschow, and P. Burlet, *J. Magn. Magn. Mater.* **104-107**, 21 (1992); R. A. Robinson, A. C. Lawson, V. Sechovský, L. Havela, Y. Kergadallan, H. Nakotte, and F. R. de Boer, *J. Alloys Comp.* **213&214**, 528 (1994).
- ²⁵C. Y. Huang, *J. Magn. Magn. Mater.* **51**, 1 (1985).
- ²⁶H. Nakotte, F. R. de Boer, L. Havela, P. Svoboda, V. Sechovský, Y. Kergadallan, J. C. Spirlet, and J. Rebizant, *J. Appl. Phys.* **73**, 6554 (1993).
- ²⁷A. J. Arko, M. B. Brodsky, and W. J. Nellis, *Phys. Rev. B* **5**, 4564 (1972).
- ²⁸R. Troć, V. H. Tran, F. G. Vagizov, I. M. Reznik, and L. Shlyk, *Physica B* **199&200**, 647 (1994).
- ²⁹P. Haen, J. Flouquet, F. Lapiere, and P. Lejay, *J. Low Temp. Phys.* **67**, 391 (1987).
- ³⁰A. V. Andreev, H. Aruga Katori, and T. Goto, *J. Alloys Compd.* **224**, 117 (1995).
- ³¹J. Kondo, *Prog. Theor. Phys.* **32**, 37 (1964).
- ³²S. Doniach, *Physica B* **91**, 231 (1977).
- ³³L. Havela, A. V. Andreev, V. Sechovský, I. K. Kozlovskaya, P. Jevorsky, M. I. Bartashevich, T. Goto, and K. Kamishima, *Physica B* (to be published).
- ³⁴S. A. M. Mentink, A. Drost, G. J. Nieuwenhuys, E. Frikkee, A. A. Menovsky, and J. A. Mydosh, *Phys. Rev. Lett.* **73**, 1031 (1994).
- ³⁵S. A. M. Mentink, G. J. Nieuwenhuys, H. Nakotte, A. A. Menovsky, A. Drost, E. Frikkee, and J. A. Mydosh, *Phys. Rev. B* **51**, 11 567 (1995).