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Magnetic properties of non-stoichiometric UNiGa

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Abstract

Magnetization measurements of alloys based on the intermetallic compound UNiGa with deviation from the exact 1:1:1 stoichiometry, namely $U_x(Ni_{0.5}Ga_{0.5})_{3-x}$ with $0.8 \leqslant x \leqslant 1.2$ and $UNi_{1.1}Ga$, have been performed. The obtained results suggest that the antiferromagnetic ground state of UNiGa can be easily transformed into a ferromagnetic one not only by external magnetic fields but also by changes of the composition.

Keywords: Uranium intermetallics; Magnetic properties

1. Introduction

The ternary uranium compound UNiGa crystallizes in the hexagonal crystal structure of the ZrNiAl type, a ternary variant of the Fe_2P structure type (space group P$\bar{6}$m2) [1]. The unit cell of the structure is shown in Fig. 1. This compound (together with UCoGa) was the first representative of the large UTX family (T is a late transition metal, X is a *p*-metal), whose magnetic properties were studied in detail [2–12]. All the studies reported a huge uniaxial magnetic anisotropy and the ordering temperature in the range 38–41 K in UNiGa. However, there was a disagreement on the type of magnetic ordering.

The first studies made on single crystals, grown at the Ural State University by a modified Bridgman technique in an alumina crucible, revealed that UNiGa is a ferromagnet. The evidence for the ferromagnetic (F) arrangement of magnetic moments was a rectangular hysteresis loop for fields along the *c*-axis with practically 100% remanent magnetization and high coercive field, observed at $T = 4.2$ K [2–4]. Moreover, the hysteresis behaviour is found to be in agreement with the model based on the pinning of narrow domain walls in ferromagnets. On the other hand, the polycrystalline UNiGa precursor for these single crystals showed no remanent magnetization, despite the fact that it also

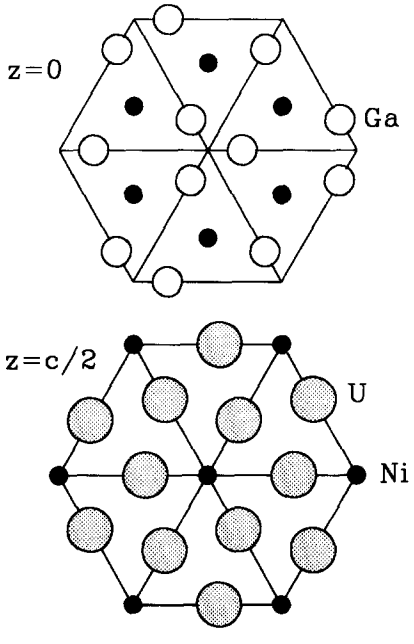

Fig. 1. Crystal structure of UNiGa.

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exhibits a large hysteresis [4]. A similar "wasp-tailed" hysteresis loop was observed on polycrystalline UNiGa in [5] and has been interpreted as a metamagnetic transition in an antiferromagnet. After this initial period, single crystals of UNiGa were grown in a tri-arc Czochralski equipment of FOM ALMOS at the University of Amsterdam [13] from a stoichiometric melt [6]. A microprobe analysis confirmed the 1:1:1 composition of the crystals. Magnetization measurements showed a clear metamagnetic transition at about 0.8 T, which was accompanied by certain hysteresis at low temperatures, but there was clearly no remanent magnetization. Also cooling in fields below about 0.5 T shows, after passing through different magnetic phases below the ordering temperature, a condensation to a phase with zero spontaneous magnetization. This behaviour was elucidated by neutron diffraction experiments showing that UNiGa orders in incommensurate antiferromagnetic structure at $T_N = 39.5$ K and undergoes three order–order transitions below this temperature. All the structures are collinear with moments along the [001] direction and antiferromagnetic in zero field. In the ground state the U magnetic moments of 1.4 μ_B are coupled ferromagnetically within the (001) layers with antiferromagnetic stacking of the $(+ + - + - -)$ type along the c-axis [10,11].

The metamagnetic transition below $B = 1$ T becomes manifest in pronounced magnetoresistance [7], magnetocaloric [8] and magnetoelastic [9] effects (there should not be noticeable effects in the case of domain wall movement in a uniaxial ferromagnet). This transition from the antiferromagnetic to the ferromagnetic state has been confirmed also directly by neutron diffraction studies [10,11].

As can be deduced from the relatively small value of the critical field, corresponding to energies much smaller than the effective exchange energy, the effective interlayer antiferromagnetic interaction is much weaker than the ferromagnetic coupling within basal plane layers.

Coming back to the results obtained on the first single crystal, we would like to explain the origin of the full remanence, pointing to a possibly ferromagnetic ground state.

The appearance of ferromagnetism in the first single crystal [2–4] cannot be explained by a contamination of the sample by Al due to reaction with a crucible, because the Al substitution for Ga leads to a sharp increase of the metamagnetic transition field, i.e. it supports antiferromagnetism [14]. Another reason can be a deviation of the composition from the exact 1:1:1 stoichiometry, which cannot be excluded during melting procedure. As the crystals studied in Refs. [2–4] were of single phase, we supposed that UNiGa has a homogeneity range with strong dependence of magnetic properties on the composition.

The aim of the present study was to check this possibility by detailed studies in the $U_x(Ni_{0.5}Ga_{0.5})_{3-x}$ cross-section of the U–Ni–Ga ternary system. The alloy $UNi_{1.1}Ga$ with extra Ni content was investigated, as well.

2. Experimental details

$U_x(Ni_{0.5}Ga_{0.5})_{3-x}$ samples of about 3 g with nominal compositions corresponding to $0.8 \leqslant x \leqslant 1.2$ have been prepared by melting the components (U purity 99.8%; Ni and Ga 99.99%) in an arc furnace on a water-cooled copper bottom under argon atmosphere. The ingots were turned several times to avoid inhomogeneities. The samples were measured in the as-cast form, because the ferromagnetic single crystals mentioned above were also not subjected to any further heat treatment after preparation. In addition, we have prepared an alloy with a higher Ni content, having the nominal composition $UNi_{1.1}Ga$. The lattice parameters were determined by a standard X-ray diffraction method.

The magnetization was measured on polycrystalline bulk pieces (20–50 mg) in a vibrating sample magnetometer at 4.2 K in steady magnetic fields up to 2 T. The magnetization of these samples was anisotropic and the magnetic field was applied along the direction of the maximum magnetization. In order to determine reliable values of the magnetic moment, the magnetization was also measured on powders composed of 50 μm-sized particles free to rotate in applied field in long-pulse field (1 s) up to 40 T at 4.2 K.

The ordering temperature was determined from temperature dependences of the *ac* susceptibility in field of the 1 mT amplitude.

3. Results and discussion

X-ray analysis showed that most of the samples are close to the single-phase state, the amount of extraneous phases not exceeding 5% for $0.9 \leqslant x \leqslant 1.1$. The sample $U_{1.2}Ni_{0.9}Ga_{0.9}$ (with $x = 1.2$), containing about 10% of spurious phases, is considered as representing the limit of the homogeneity range. On the other hand, the sample prepared with $x = 0.8$ is certainly outside the homogeneity range, because it contains more than 40% of impurity phases. The $UNi_{1.1}Ga$ alloy is single phase.

Fig. 2 presents dependences of the lattice parameters a and c on the U content x in the $U_x(Ni_{0.5}Ga_{0.5})_{3-x}$ cross-section of the homogeneity range. Despite the fact that U has a larger metallic radius than Ni and Ga, both lattice parameters decrease with increasing U content. However, the variation of the lattice parameters is relatively small. A similar wide homogeneity range with low sensitivity of lattice parameters to the

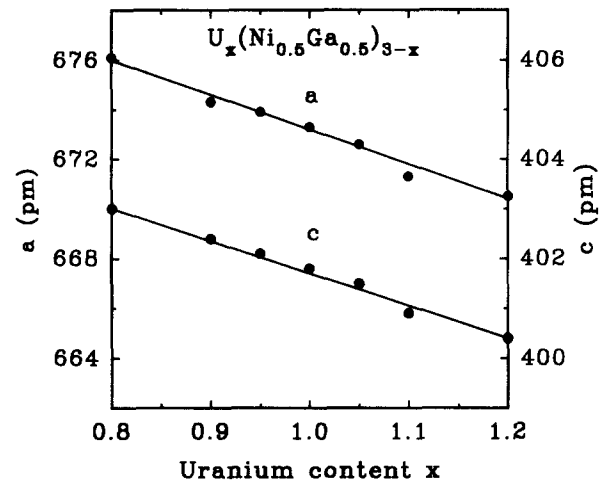

Fig. 2. Concentration dependence of lattice parameters in the $U_x(Ni_{0.5}Ga_{0.5})_{3-x}$ system.

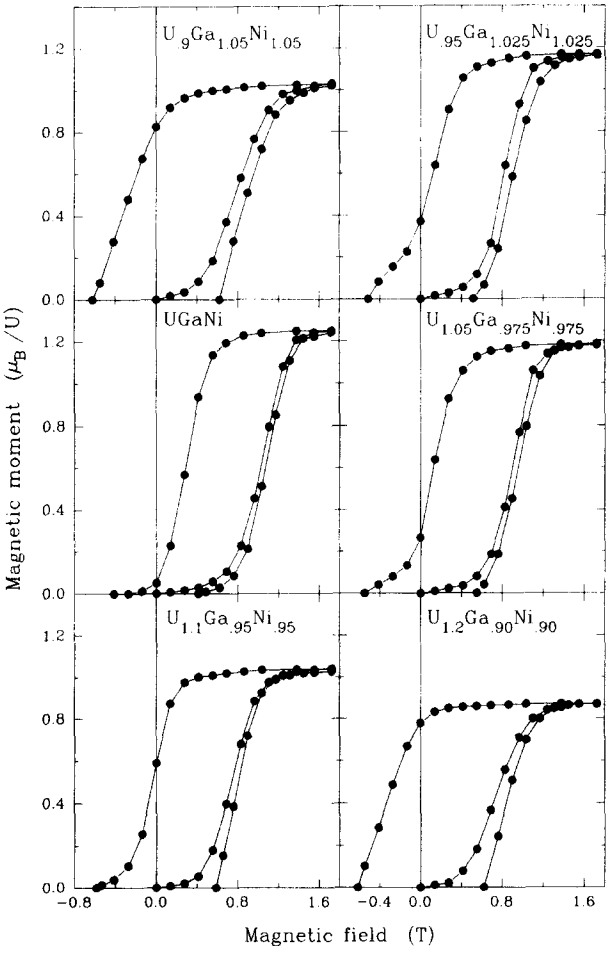

Fig. 3. Virgin magnetization curves and hysteresis loops along the c-axis of the $U_x(Ni_{0.5}Ga_{0.5})_{3-x}$ system at $T=4.2$ K.

non-stoichiometry has been observed also in another UTX system, $U_x(Co_{0.5}Al_{0.5})_{3-x}$ [15].

Virgin magnetization curves and hysteresis loops, obtained on bulk samples, are shown in Fig. 3. The maximum magnetization obtained on "anisotropic" bulk pieces reaches about 90% of the free-powder value. Therefore, the data presented in Fig. 3 practically correspond to single crystals measured with the field applied along the c-direction, the latter being the easy magnetization direction in UNiGa and all related UTX compounds. Stoichiometric UNiGa has a very low remanent magnetization: the hysteresis loop is practically the same as observed for polycrystals in Refs. [4,5] and is similar to the single-crystal loop of Ref. [6], i.e. is pertinent to an antiferromagnet. With increasing deviation from the 1:1:1 stoichiometry, the remanent magnetization increases, and finally the hysteresis loops become typical for ferromagnets affected by strong domain-wall pinning ($x=0.9$ and 1.2). Based on the magnetization curves of the samples with $x=0.95$, 1.05 and 1.1, one may speculate that here the antiferromagnetic and ferromagnetic phases coexist. The coercivity is equal to about 0.7 T for all the samples containing a ferromagnetic contribution within the $U_x(Ni_{0.5}Ga_{0.5})_{3-x}$ cross-section of the homogeneity range. The sample with the extra Ni content, $UNi_{1.1}Ga$, is a ferromagnet and the coercivity reaches 1.3 T (Fig. 4).

Two possibilities can be considered to explain the high remanence of the non-stoichiometric samples. The first one is that the ground state is always antiferromagnetic. In that case the high-magnetization state induced by fields exceeding the metamagnetic field persists due to the fact that the hysteresis loops extend to both sides of $B=0$. The origin of this effect can be seen in lattice defects (antistructure atoms) induced by the off-stoichiometry.

The second possibility is that the true ferromagnetic phase is stabilized in zero field, which means that the weak antiferromagnetic interlayer coupling is changed to the ferromagnetic one as a consequence of the change of the occupation of particular atomic sites.

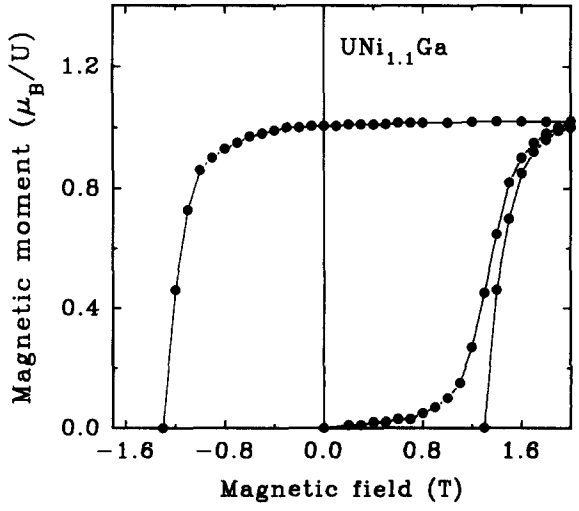

Fig. 4. Virgin magnetization curve and hysteresis loop along the c-axis of $UNi_{1.1}Ga$ at $T=4.2$ K.

We can expect, for example, an important role of the U atoms appearing between the U–T layers due to the atomic disorder.

In the following we can see that the results of magnetostriction and thermal expansion measurements point to the latter case.

Fig. 5 shows magnetization and magnetostriction curves measured on the stoichiometric single crystal [6,9]. One can see that the metamagnetic transition is accompanied by a relatively weak but well noticeable magnetostriction effect. The crystal shrinks under the influence of magnetic field along the c-axis and expands in the basal plane. The longitudinal $\lambda_{\parallel}$ and the transversal $\lambda_{\perp}$ magnetostriction strains reach the values of -2.1×10^{-4} and 1.0×10^{-4} respectively. The volume effect $\omega=\lambda_{\parallel}+2\lambda_{\perp}$ is by at least one order of magnitude smaller due to practically complete cancellation of the linear strains. This magnetostriction effect cannot be explained by magnetization processes in a ferromagnet, because there is, due to the symmetry reasons, no magnetostriction during 180° domain wall movement in an uniaxial ferromagnet.

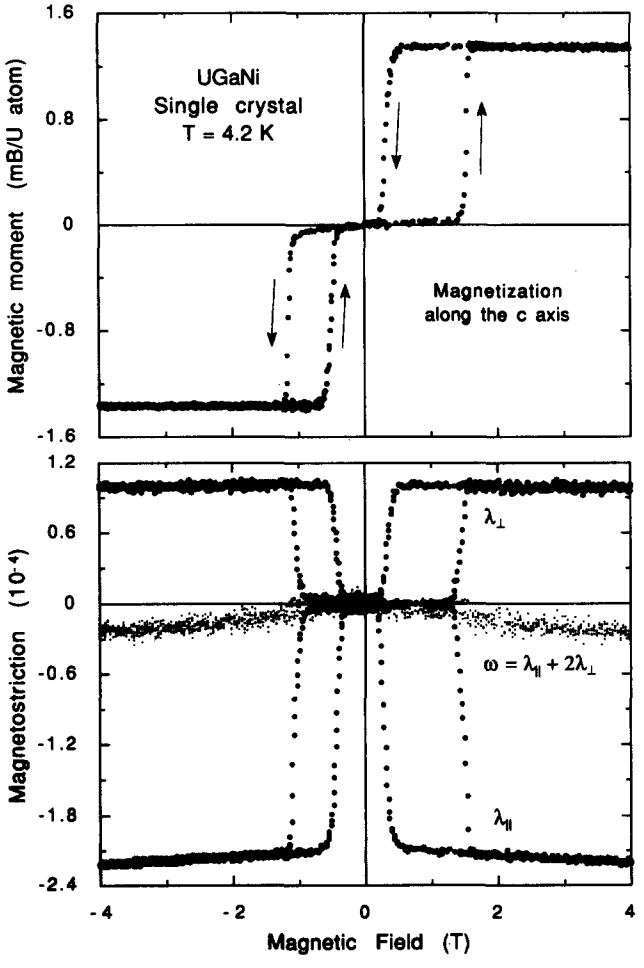

Fig. 5. Field dependences of the magnetization (top) and magnetostriction (bottom) of the stoichiometric UNiGa single crystal at $T=4.2$ K.

In the case of the non-stoichiometric compound $UNi_{1.1}Ga$, both the magnetization and demagnetization processes shown in Fig. 4 are not accompanied by any noticeable magnetostriction effects. This points undoubtedly to the stability of the ferromagnetic state in $B=0$.

Although we do not know the exact composition of the original single crystal, we can deduce that also here the ground state was ferromagnetic. There is a close connection between the magnetostriction results and the thermal expansion data, available for both crystals, which are shown in Fig. 6. The lines correspond to the original ferromagnetic single crystal [4], and the circles to the antiferromagnetic crystal. Above 50 K, the a- and c-parameters of the ferromagnetic sample are larger by 0.5 pm and 0.3 pm respectively. This difference is practically within the experimental accuracy of determination of a and c. For the clarity of presentation, the $a(T)$ and $c(T)$ curves of the ferromagnetic sample were matched at 50 K with values of the antiferromagnetic sample. The thermal expansion of both samples follows practically the same temperature dependence in the range 50–300 K. The temperature dependence of the unit-cell volume can be described using the Debye model with the Debye temperature $\Theta_D=(200\pm30)$ K, which is consistent with $\Theta_D=185$ K obtained from the specific-heat measurements [8]. A difference in the thermal expansion appears with the onset of magnetic ordering. While the ferromagnetic sample yields no anomaly, the lattice parameter c of the antiferromagnetic sample slightly increases below about 40 K and a shows a decrease, cancelling any volume effect. Comparing the respective curves, we can

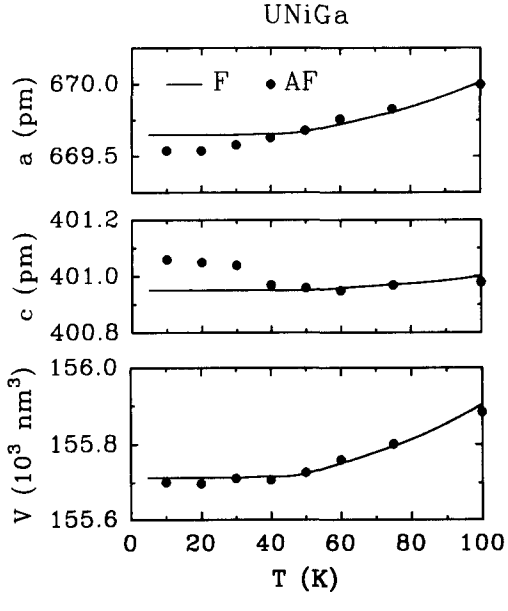

Fig. 6. Temperature dependences of the lattice parameters a and c and the unit-cell volume V for ferromagnetic (lines) and antiferromagnetic (circles) single crystals.

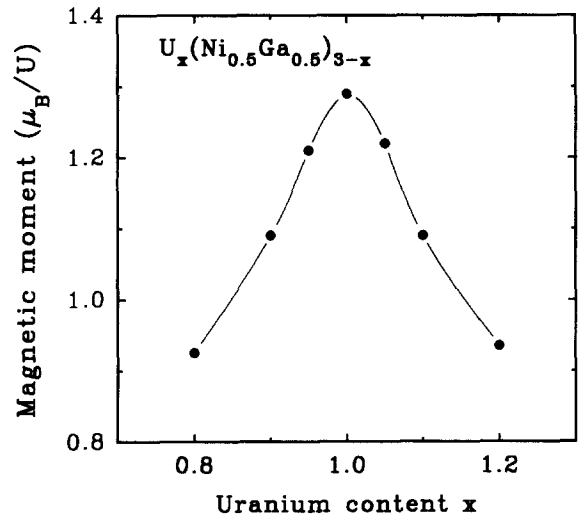

Fig. 7. Concentration dependence of the U magnetic moment in the $U_x(Ni_{0.5}Ga_{0.5})_{3-x}$ system at $T=4.2$ K obtained from free powder measurements.

evaluate effective magnetostriction effects yielding the coefficients $\lambda_a = -(1.5 \pm 0.5) \times 10^{-4}$ and $\lambda_c = (2.5 \pm 0.5) \times 10^{-4}$ (at 10 K). They correspond well to values of $\lambda_\parallel$ and $\lambda_\perp$ mentioned above ($\lambda_a = -\lambda_\perp$, $\lambda_c = -\lambda_\parallel$). Since the thermal expansion of the ferromagnetic crystal was measured in zero magnetic field, the ferromagnetic state is undoubtedly the ground state of this sample.

The saturation moment per U atom, found from the extrapolation of the magnetization curve of the free powder sample (with single crystalline particles) to zero field, reaches 1.3 μ_B in the stoichiometric sample, which is in agreement with 1.35 μ_B observed in the single crystal [6]. (Note that the magnetization in UTX compounds is carried predominantly by U-moments [12].) Fig. 7 shows the concentration dependence of the U moments in the $U_x(Ni_{0.5}Ga_{0.5})_{3-x}$ alloys at 4.2 K obtained from free powder measurements. The U moment decreases considerably with the deviation of the stoichiometry from the ideal 1:1:1 one, independent of whether it is connected with a deficiency or an excess of U. On the other hand, the ordering temperature is found to be about the same (38 K) for the whole $U_x(Ni_{0.5}Ga_{0.5})_{3-x}$ series. This shows that the exchange energy is determined mainly by the strong intralayer ferromagnetic interactions, which are not sensitive to the atomic disorder to a certain extent.

4. Conclusion

We have found a rather wide concentration range of stability of the intermetallic compound UNiGa which allows at least 10% off-stoichiometry while preserving the crystal structure. Although the "ideal" UNiGa is antiferromagnetic, any off-stoichiometry drives the system towards ferromagnetism. Moreover, the deviation from the 1:1:1 stoichiometry leads to a reduction of the ordered magnetic moment. The magnetic ordering temperature of about 38 K, however, remains unaffected. Ferromagnetism and the reduced U moment found in early studies of UNiGa single crystals can be explained in this way by a shift of composition during the single-crystal growth. For an ultimate proof of these findings, however, the neutron diffraction studies are considered.

Acknowledgments

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