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Magnetic first-order transitions in UNiGe

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Abstract. Bulk magnetic and neutron diffraction measurements revealed that UNiGe orders antiferromagnetically at $T_N = (43.3 \pm 0.1)$K. The magnetic unit cell is doubled along the a and c directions corresponding to a propagation vector $k = (\frac{1}{2}, 0, \frac{1}{2})$. At 13 K the ordered magnetic moment of uranium amounts to $(1.37 \pm 0.07)\mu_B$ and is aligned along the b axis. There is strong experimental evidence that the transition to the ordered state is of first order.

1. Introduction

The structural, thermodynamical and other physical properties of intermetallic compounds with the general formula UTX (where T is a 3d or a 4d metal and X = Al, Ga, Sn, Si and Ge have been of intense interest during the recent few years (Troć 1986, Andreev and Bartashevich 1986, Sechovski *et al* 1986, Palstra *et al* 1987). These ternary uranium compounds exhibit a variety of interesting magnetic properties, such as itinerant or localized magnetism, spin fluctuations, Kondo lattice and possible heavy-electron behaviour. Most of them crystallize in the body-centred $CeCu_2$ type structure (space group Imm$a$), in which the uranium atoms occupy the (4e) cerium positions: $\pm(0, \frac{1}{4}, z_U)$, whereas the transition and metalloid atoms are on (8h) copper sites, i.e. on $\pm(0, y, z)$ and $\pm(0, \frac{1}{2} + y, \bar{z})$. Exact values of the positions of the uranium and transition metal (metalloid) atoms have not been determined so far.

Comprehensive x-ray and bulk magnetic susceptibility measurements were performed previously on 14 equiatomic ternary UTX intermetallics by Troć and Tran (1988). Most of these compounds (except UCoSi and UCoGe) have shown a phase transition to the magnetic ordered state at low temperatures. A sharp maximum in the susceptibility observed by the above mentioned authors at 44 K for UNiGe suggests a first-order transition to an antiferromagnetic state. At this temperature, a distinct anomaly has also been detected by the electrical resistivity measurements (Tran *et al* 1990). On the other hand, it is worth noting that the value of the U–U distance in UNiGe of about 3.54 Å lies just on the Hill limit. For uranium compounds a Hill plot is frequently used as a guide to decide whether one is concerned with more localized 5f electrons (which implies a magnetic order at low temperatures) or rather with the itinerant behaviour of the non-magnetic 5f/6d (non-magnetic state). In view of the short U–U distance in UNiGe and the observed anomaly in the susceptibility and electrical resistivity measurements, indicating a transition to an antiferromagnetic state, one may expect 5f electrons to be somewhat intermediate between itinerant and localized.

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The purpose of the present neutron diffraction study is to obtain, on an atomic scale, insight into the low-temperature magnetic behaviour of this compound and to refine its structural parameters.

2. Experiment

The UNiGe specimen was obtained by arc melting of constituents with 1:1:1 stoichiometry under an argon atmosphere. After the annealing of the sample at 650 °C for two weeks under a vacuum, the powder x-ray diffraction pattern proved that the sample had the proper $CeCu_2$-type crystal structure.

Neutron diffraction experiments were carried out at the Saphir reactor, Paul Scherrer Institute at Villigen, using the multidetector powder diffractometer DMC (Schefer *et al* 1990) and a two-axis diffractometer of Labor für Neutronenstreuung ETHZ. For the analysis of crystal and magnetic structures, the neutron diffraction patterns were recorded with neutrons of wavelength $\lambda = 1.704$ Å (Ge (311) monochromator, liquid nitrogen cooled Si filter) at 50 and 13 K, using a closed-cycle helium refrigerator. The temperature variation of the magnetic peak intensity was measured on the two-axis diffractometer with a neutron wavelength $\lambda = 2.34$ Å (pyrolytic graphite monochromator and filter). The Rietveld profile method modified by Hewat (1979) was applied to analyse the neutron diagrams, based on the neutron scattering lengths $b_U = 8.42$ fm, $b_{Ni} = 10.3$ fm and $b_{Ge} = 8.18$ fm. The neutron scattering lengths were taken from Sears (1986). The magnetic form factors of uranium were taken in the dipole approximation after Freeman *et al* (1976).

3. Neutron diffraction results and analysis

The neutron powder diffractogram of UNiGe taken at 50 K (cf figure 1) was completely indexed on the basis of an orthorhombic body-centred unit cell. Nevertheless, small traces of impurities were also detected. Apart from a few very weak peaks, which were recognized as being due to the presence of Ge, Ni and UO_2, the lattice parameters (cf table 1), powder intensities and observed extinction rules (appearance of only $h + k + l = 2n$ peaks) indicate a strongly structural analogy of UNiGe with the crystal structure of $CeCu_2$. The Rietveld profile fitting procedure yielded, after few refinement cycles, the reliability factor for integrated intensities $R_{In} = 5.7\%$, assuming 4U on 4e-sites and a statistical distribution of Ni + Ge on the 8h-sites of space group Imm*a*. The refined structural parameters are summarized in table 1.

Compared with the 50 K diagram, the neutron diffraction pattern of UNiGe measured at 13 K up to an angle $2\Theta = 85°$ shows, at the low-angle part, the presence of additional, very weak peaks (figure 2) resulting from the magnetic ordering. They can be readily indexed on the basis of a magnetic unit cell with lattice constants $a_m = 2a$, $b_m = b$ and $c_m = 2c$ (propagation vector $k = (\frac{1}{2}, 0, \frac{1}{2})$). The appearance of magnetic peaks with the Miller indices h and $l = 2n + 1$ proves that moments at x, y, z and $x + \frac{1}{2}, y, z$ or $x, y, z + \frac{1}{2}$ of the magnetic unit cell are coupled antiferromagnetically. The observed magnetic peaks follows the rule: $h + 2k + l = 4n$ where n is an integer. The simplest hypothesis to fulfil this requirement is to assume that the uranium moments at positions: $0, \frac{1}{4}, z$ and $0, \frac{3}{4}, \bar{z}$ as well as at positions: $\frac{1}{2}, \frac{3}{4}, z + \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{4}, \bar{z} + \frac{1}{2}$ of the chemical unit cell (cf figure 3) form a collinear arrangement with the following relative orientation:

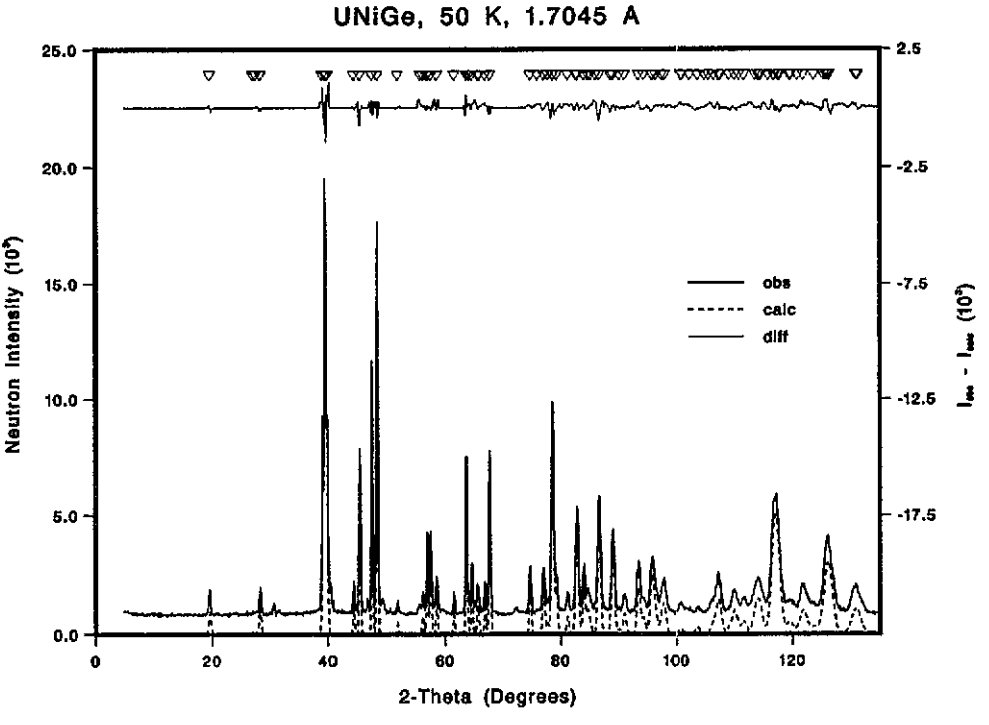

Figure 1. Observed (full curve) and calculated (broken curve) neutron diffraction patterns of paramagnetic UNiGe at $T = 50$ K. The positions of nuclear reflections are indicated by open triangles at the top of figure.

Table 1. Lattice parameters (in Å) and structural parameters of UNiGe. For refined parameters the number in parentheses represents the estimated standard deviation, ESD, of the last significant digit. The lattice constants determined at 293 K in earlier x-ray measurements (Troć and Tran 1988) are also shown for comparison.

	T(K)		
	293	50	13
a	4.238	4.2367(2)	4.2388(4)
b	7.002	6.9732(3)	6.9738(6)
c	7.206	7.1694(4)	7.1663(7)
x_U		0	
y_U		0.25	
z_U		0.5447(3)	
x_{Ni}		0	
y_{Ni}		0.0531(2)	
z_{Ni}		0.1653(2)	
x_{Ge}		0	
y_{Ge}		0.0531(2)	
z_{Ge}		0.1653(2)	
B_U		0.0(1)	
B_{Ni}		0.1(1)	
B_{Ge}		0.1(1)	

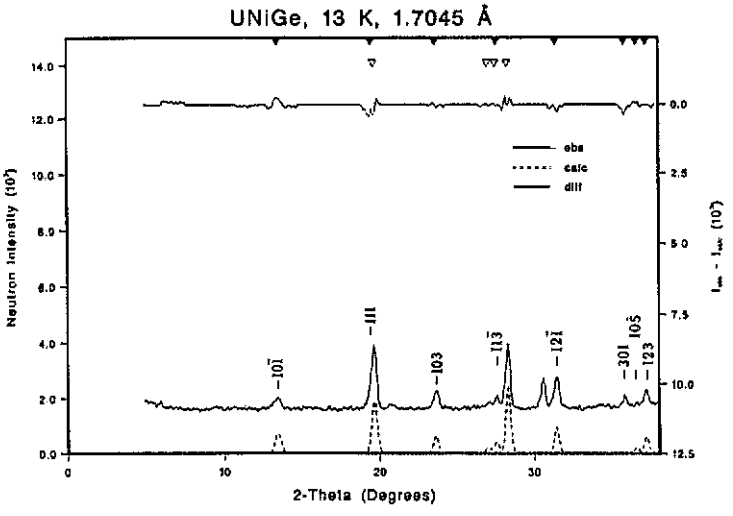

Figure 2. The low-angle part of the neutron pattern taken at 13 K. Note the presence of very weak peaks of magnetic origin in the 13 K diagram. The positions of nuclear and magnetic reflections are indicated by open and closed triangles, respectively, at the top of figure. The magnetic peaks are indexed in an enlarged unit cell as described in the text.

$+ - + -$. The whole structure can be then reproduced by applying the anti-translation operation along the a and c axes. To refine the magnetic structure, the Rietveld profile fitting procedure has again been applied allowing only for the variation of lattice parameters and the value of magnetic moment and its direction with respect to lattice axes. Structural parameters resulting from the 50 K fit were kept constant and the nuclear peaks were included in the calculation to obtain the scale factor. The fitting of magnetic intensities was, however, complicated by the fact that two out of eight observed magnetic peaks, namely M(121) and M(301), were contaminated by the UO_2(111) and Ge(200) impurities. In the case of M(301) the Ge(200) contamination, as proved by comparing with the 50 K diagram, was relatively large. In addition, the overlapping M(111) peak with the nuclear (012) one reduced severely the number of independent observables. After correction of the M(121) intensity for contamination of UO_2(111), which was achieved by subtraction of the observed intensity at 50 K, seven reflections were used in the fitting procedure. The intensities of the magnetic peaks as a function of the magnitude of the momentum transfer Q appeared to decrease in approximate accordance with a squared U^{4+} or U^{3+} form factor (Freeman *et al* 1976). It was, therefore, reasonable to assume that the magnetic scattering arises from antiferromagnetically ordered magnetic moments due to 5f electrons. Due to the relatively small amount of data, models with non-collinear arrangement of magnetic moments were not tried.

The best agreement (agreement of integrated magnetic intensities $R_{Im} \simeq 17\%$) between calculated and observed intensities was achieved for the magnetic moment equal to $\mu_U = (1.37 \pm 0.07)\mu_B$ oriented along the a axis. Results of fitting are shown in figure 2 where calculated and observed magnetic intensities are displayed on an enlarged scale. Table 2 shows the comparison between observed and calculated integrated intensities resulting from the fit. The model of magnetic ordering is sketched in figure 3. In order to determine the Néel temperature and the sublattice magnetization with respect to T, we have measured the temperature variation of the integrated intensity of the largest magnetic peak M(121). This was achieved using a two-axis diffractometer and by replacing all vanadium radiation shields by aluminium ones.

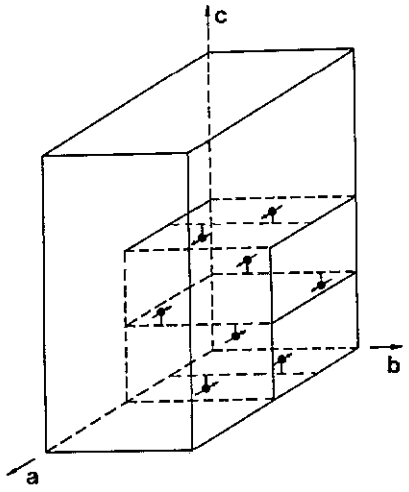

Figure 3. Perspective view of the (2a, b, 2c) magnetic unit cell of UNiGe. For sake of clarity, only positions of uranium atoms and the magnetic moment arrangement in the chemical unit cell are displayed.

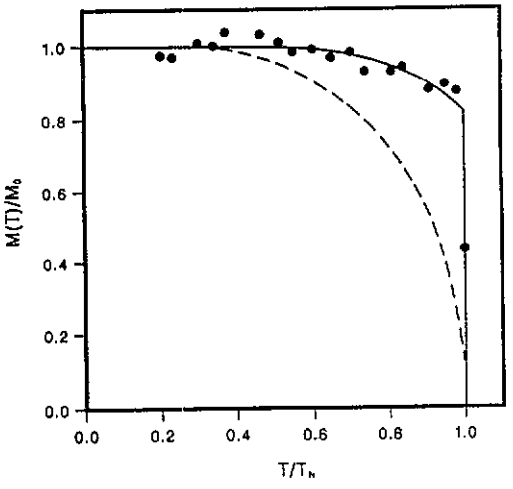

Figure 4. Temperature dependence of sublattice magnetization derived from magnetic intensity M(121). The solid curve represents the course of magnetization calculated on the basis of Bean and Rodbell theory as described in the text. The broken curve is the calculated sublattice magnetization for spin $S = \frac{1}{2}$ for the case of a rigid lattice.

Table 2. Observed and calculated integrated magnetic intensities of UNiGe resulting from the Rietveld fitting procedure.

hkl	I_{obs}	I_{calc}
$10\bar{1}$	3110	3395
111	500	154
103	2678	2511
$11\bar{3}$	794	768
$12\bar{1}$	4498	3472
$10\bar{5}$	779	736
123	2600	2022

Results of measurements are shown in figure 4. The remarkable feature of zero-field magnetization variation with temperature is an abrupt drop yielding $T_N = (43.3 \pm 0.1)$K. The broken curve in this figure represents the temperature behaviour of zero-field magnetization calculated in a molecular field approximation for the case of spin $\frac{1}{2}$. As is obvious from the figure, the experimentally observed curve deviates essentially from that predicted for $s = \frac{1}{2}$ and near T_N its behaviour resembles that characteristic of a first-order transition. The question remains as to the origin and nature of this transition in UNiGe. Within instrumental resolution we did not detect any change of crystal symmetry at T_N. Insufficient information about the parameters for $T = 13$ K leaves the question open as to whether there are any deviations of atomic coordinates at 13 K from those determined at 50 K. Indirectly, judging from the reliability factors R_I for nuclear reflections at 50 K (for the range 2Θ (5–130) deg: $R_{In} = 5.7\%$) and for nuclear reflections at 13 K (in the range of 2Θ (5–85) deg: $R_{In} = 5.7\%$) one may conclude

that the eventual deviations are not severe. The problem of the conditions required for a magnetic phase transition to be of first order has been studied in detail by Bean and Rodbell (1962) in the molecular field approximation. They have shown that if the lattice is deformable, the change of magnetization with temperature depends upon the steepness of the exchange interaction dependence on lattice volume and compressibility. The corresponding expression for the magnetization has been given by authors (cf equation (4)) as:

$$T/T_0 = (\sigma/\tanh \sigma^{-1})(1 + \eta\sigma^2/3 - PK\beta)$$

with $\eta = 3/2NkT_0\beta$ where β is the slope of the dependence of the phase transition temperature on cell volume, P is the pressure, K the compressibility, σ the relative magnetization and T_0 the temperature of the magnetic phase transition for the lattice to be incompressible. N is the number of magnetic ions per unit volume and k is the Boltzmann constant. The above expression for $\eta = 1.7$ with the applied pressure P set to zero is plotted in figure 4 as a full curve. It fits the experimental points rather well, supporting the conclusion that this transition is of first order. We expect that further experimental investigations on the family of isostructural compounds UTX will provide more experimental evidence on the nature of this transition. This assumption is reinforced by the susceptibility data (Troć and Tran 1988) which suggests that a similar antiferromagnetic first-order transition occurs in UNiSi.

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