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Abstract
The effect of uniaxial pressure on the magnetic ordering in a single-crystalline sample of UNiAl has been studied by means of neutron diffraction. The crystal and magnetic structures remain in a first approximation unaffected for the pressure applied along the c axis. For perpendicularly applied pressure, severe changes to the magnetic ordering are found. From the original six magnetic reflections that are associated with each nuclear reflection, two disappear and the remaining four rotate in the reciprocal plane, marking modification of the propagation vector. The U magnetic moments are reduced upon application of the pressure along the a axis, by about 0.11 μ_B kbar^{-1}. In contrast, the magnetic phase transition temperature increases by about 0.6 K kbar^{-1}. The results are explained qualitatively in terms of pressure-induced changes of exchange interactions.

1. Introduction

Among 5f electron systems, equiatomic UTX (T = late transition metal; X = p electron element) compounds crystallizing in several distinct crystal structures [1] belong to the group that are most studied [1, 2]. Due to the anisotropy in the bonding of 5f electrons, very strong hybridization-induced magnetocrystalline anisotropy is quite common in these materials. The participation of the 5f electron states in the bonding inevitably leads to their delocalization and, in the limit of strong hybridization, to destruction of long-range magnetic order. As the hybridization depends on the overlap of 5f states with ligand electron states, the applied pressure can effectively control it. This, in turn, modifies the effective magnetic interactions between 5f electrons and can lead to an increase of the magnetic phase transitions before it delocalizes the 5f states completely.

UNiAl forms in the hexagonal ZrNiAl-type structure, in which U atoms occupy the 3(g) x_U, 0, 0.5 ($x_U \approx 0.58$) position. We denote a U atom at x_U, 0, 0.5 as U$_1$, at 0, x_U, 0.5 as U$_2$ and at $1 - x_U$, $1 - x_U$, 0.5 as U$_3$. UNiAl orders antiferromagnetically (AF) below $T_N = 19.3$ K and exhibits uniaxial magnetic anisotropy [3]. The c axis is the easy-magnetization direction. There are three equivalent propagation vectors that describe the AF order. For zero field and ambient pressure we denote these vectors as $q_1 = (0.1\ 0.1\ 0.5)$, $q_2 = (-0.1\ 0.2\ 0.5)$, and $q_3 = (-0.2\ 0.1\ 0.5)$ [4]. A small non-zero temperature dependence of the length of these vectors proves that the magnetic structure is incommensurate [5]. It was suggested that for UNiAl one deals with three domains, each having just one propagation vector [4]. U moments are sine-wave modulated within the basal plane and coupled AF with U moments in the adjacent plane along the c axis. All three U magnetic moments are oriented along the hexagonal axis and the maximum size on U$_1$ and U$_2$ positions is 1.25 μ_B. The third moment U$_3$ carries a smaller moment.

Interestingly, upon application of magnetic field higher than 8 T applied along the easy-magnetization direction of UNiAl, uniform 'rotation' of magnetic reflections by 30° has been observed from positions determined by $q = (0.1\ 0.1\ 0.5)$ towards the propagation vector $(0.173\ 0\ 0.5)$ [6]. The exact mechanism for the phase transformation remains, however, unknown. The length of the propagation remains the same.

Although the application of hydrostatic pressure causes drastic changes in the electrical resistivity at low temperatures [7], the AF structure remains unaltered [8]. One merely finds that the U moment magnitudes decrease with increasing pressure. Eventually, the magnetic order in UNiAl collapses at hydrostatic pressures of the order of 6–10 GPa [9, 10]. This is easily understood in terms of increasing delocalization of the 5f states. However, it is also known that uniaxial pressure on anisotropic materials can have the completely opposite effect. As an example one can cite a pressure-induced ferromagnetic order in originally metamagnetic and isostructural UCoAl [11].

2. Experimental details

The single crystal of UNiAl used in the present study originates from the same large crystal as was used in previous studies [4, 8]. A cube with dimensions $3.2 \times 3.2 \times 3.2$ mm^3 was carefully cut and polished to have plane-parallel faces. The integrated intensities were measured using the flat-cone E2 diffractometer installed at the Helmholtz Center in Berlin in two subsequent experiments, with an incident neutron wavelength of 2.4 Å. The crystal was mounted in both cases with its hexagonal axis vertical. While in the case of nuclear reflections we were confined to the $(hk0)$ reflections, the flat-cone option allowed us to reach magnetic (hkl) reflections with index $l = 0.5$. The two experiments differed in the direction in which we have applied a small uniaxial pressure provided by a simple home-made cell. In the first one, the pressure produced by four screws was applied along the hexagonal axis. In the second experiment, the same crystal was mounted so that the pressure was applied along the a axis.

In both experiments, measurements were made on the single crystal before applying pressure, at two or three elevated pressures in an ascending sequence, and after removing the pressure. At each particular pressure at least two large data sets were taken at low temperatures—one containing 18 nuclear reflections (half of the reciprocal plane with $l = 0$), which took typically 3 h, and the other containing up to 24 magnetic reflections (one sixth of the reciprocal plane with $l = 0.5$), which took typically 18 h. We also followed a few representative nuclear and magnetic reflections as a function of temperature in the range 1.6–30 K. The cell parameters were refined from positions of available nuclear reflections. Intensities were fitted to either Gaussian (nuclear reflections) or pseudo-Voigt (magnetic reflections) profiles. The crystallographic and magnetic structures were determined by fitting procedures using the program FULLPROF [12].

3. Results

3.1. Magnetic structure for pressure along the c axis

Due to the limited amount of measured reflections, we kept, except for the two structural parameters (the x positional parameters of the U and Al atoms x_U and x_{Al}) and the extinction parameter, all remaining variables fixed. Our refinements are in accord with literature structural parameters [4] and indicate that a significant extinction is

present in the crystal. As the pressure is increased, the intensities of all the reflections increase. It appears that the crystal structure remains unchanged at all elevated pressures and the intensity increase is due to the decreasing effect of extinction.

From the position of the measured reflections it should be possible to estimate the actual pressures. To do this, however, the compressibilities along the principal directions must be known. Unfortunately, these are not known for UNiAl and one has to estimate them. We have taken for their values average values known for UNiGa [13] (a uniaxial antiferromagnet) [14] and URhAl (a uniaxial ferromagnet) [13, 15]. Values $k_a = 3.9 \times 10^{-3}$ GPa^{-1} and $k_c = 1.6 \times 10^{-3}$ GPa^{-1} have been adopted. Because no direct observation of the (hkl) reflections with $l > 0.5$ is possible, one has to suppose for this orientation that the volume of the crystal remains unchanged. However, it appeared that no reliable estimation of the actual pressures applied along the c axis is possible. We refer therefore in the following text only to pressures P_i ($i = 0, 1, 2, 3$). The index 0 denotes the ambient pressure and the index 3 the highest pressure. It is nevertheless assumed that the pressures applied along the c and a axes are similar in magnitude.

In figure 1(a) we show some of the data converted into reciprocal space at ambient pressure and 1.6 K, resulting from the scattering plane (h k 0.5). Each nuclear reflection is associated with six magnetic reflections that can be described using three propagation vectors q_i and the associated $-q_i$. It appears that all the magnetic reflections remain present at higher pressures and, like for the case of nuclear reflections, their intensities increase. This is documented in figure 1(b) where we show profiles of magnetic reflection $(200)^{+q3} = (1.8\ 0.1\ 0.5)$ projected onto the scattering angle 2θ. In figure 1(c) the fitted parameters as a function of the pressure along the c axis are shown. It is not clear whether the shift in the position of magnetic reflections is caused by a modification of the lattice constants or due to a change in the length of the propagation vector. The resolution in the vertical direction is insufficient to allow a clear determination of the c axis parameter.

Due to the relatively low number of magnetic reflections we have constrained magnitudes at all uranium sites to be equal and merely introduced a phase shift between the relevant sites. Although not completely correct, such a modification of the model has no influence on the main conclusions. The magnitude of the U magnetic moments remains within the error bars, unaffected upon application of pressure. One merely finds that the originally differently populated domains become nearly equally populated at elevated pressures.

3.2. Magnetic structure for pressure along the a axis

In contrast to the pressure applied along the c axis, the pressure applied along the a axis has profound consequences for the physical properties of UNiAl. As the pressure is increased, the intensities of all the nuclear reflections increase due to the effect of extinction also for this orientation. It appears that the (300) reflection shifts towards higher diffraction angles whereas the (−210) reflection, which makes with the
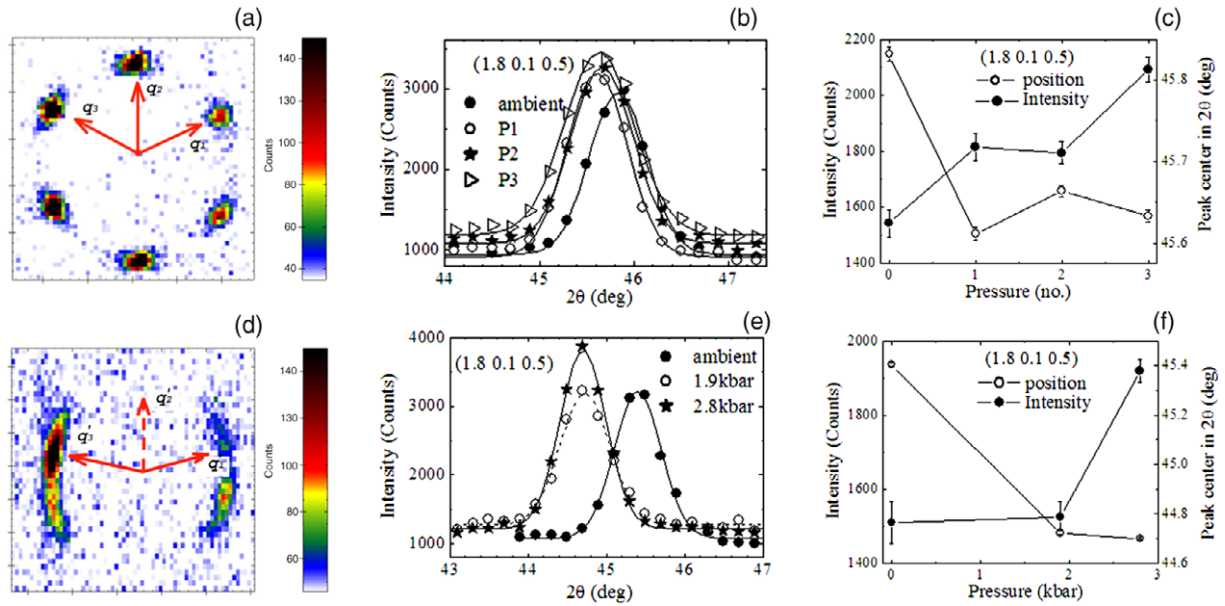
Figure 1. Portion of a typical data set containing magnetic reflections of the $(200)^{+-qi}$ type converted into the reciprocal space measured at ambient pressure (a) and at the elevated pressure applied along the a axis (d). Scan profiles of the $(200)^{+q3} = (1.8\ 0.1\ 0.5)$ reflection measured at ambient pressure and three elevated pressures applied along the c axis (b) and along the a axis (e) projected onto the diffraction angle 2θ. The pressure dependence of the $(200)^{+q3}$ integrated intensity (filled points) together with its fitted position for pressure applied along the c axis (c) and along the a axis (f).

(This figure is in colour only in the electronic version)

former one a right angle and is actually equivalent to (110) reflection, shifts towards lower diffraction angles. Obviously, the crystal structure symmetry does show a small orthorhombic distortion. The actual relative deviation amounts to 0.12% at the highest pressure. Therefore, we further use the hexagonal symmetry frame system. Nevertheless, the changes in the lattice constants were large enough for determining the applied pressure. We arrived at $P_{1a} = 1.9 \pm 0.4$ kbar for the lower one and $P_{2a} = 2.8 \pm 0.5$ kbar for the second, the higher pressure.

Whereas the nuclear reflections change their position and intensity as a function of pressure rather moderately, the magnetic reflections change in a more substantial way. As an example of the measured data we show in figure 1(d) a small portion of the reciprocal space around the (2 0 0.5) position (compare with figure 1(a)) recorded at P_{2a}. Reflections that are described originally by the propagation vector $q_2 = (-0.1\ 0.2\ 0.5)$ and the associated $-q_2$ vector disappear quickly while those remaining (indexed by using q_1 and q_3 vectors) get stronger and move in the reciprocal space. The direction of the q_2 vector projected on the basal plane is identical with the direction perpendicular to the applied pressure. In figures 1(e) and (f) we show the pressure effect on the reflection that is originally identified as $(1.8\ 0.1\ 0.5) = (2\ 0\ 0)^{+q3}$. Its position 'jumps' to lower diffraction angles already at the pressure P_{1a} and simultaneously its intensity increases slightly. Further increase of the pressure to P_{2a} does not shift the reflection substantially; it causes, however, its intensity increase. It is apparent that the propagation vectors of the AF structure do not remain the same. Existing reflections 'rotate' towards the direction along which the pressure is applied. At the same time, the determination of the distance between $+q$ and associated

$-q$ reflections suggests that the length of the propagation vector increases from 0.173 r.l.u. at the ambient pressure to 0.179 and 0.185 r.l.u. in the case of P_{1a} and P_{2a}, respectively. Simple calculation shows that the propagation vector of the new AF structure reads $q'_{P1a} = (0.13, 0.07, 0.5)$ and $q'_{P2a} = (0.16, 0.04, 0.5)$ at the two elevated pressures, respectively. Let us note that we have not found any extra diffraction signal that would not be present at ambient pressure.

As no third harmonics have been detected at elevated pressures we conclude that also upon application of the pressure the magnetic structure of UNiAl remains in the form of a transverse sine-wave incommensurate type. However, as is evident from the positions of the magnetic reflections, the direction of the sine-wave modulation turns within the basal plane. At the same time, its absolute length increases, suggesting shortening of the modulation in the real space. Let us note that both (turning and stretching of the propagation vector) effects have been already observed for UNiAl, however, under other circumstances [5, 16].

Symmetry analysis (supposing the very same underlying hexagonal structure) shows that all three atomic positions should be treated independently. This, however, would lead to large error bars due to the low number of observables. We have therefore fixed magnitudes at all three sites restricted to being identical, which is consistent with the spatial fraction of the three domains (determined by vectors q'_i) and the phase shifts between the moments the only free variables. Results of the best fit of the three fit parameters to 18 observed intensities are summarized in figure 2. One of the domains vanishes very quickly and the average moment magnitude in the remaining two domains decreases substantially with
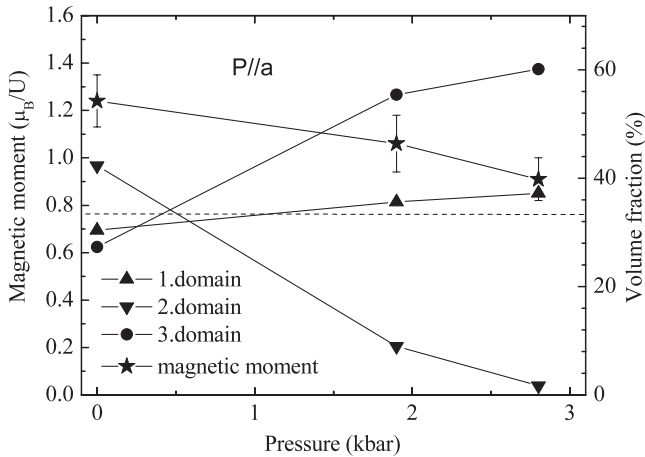
Figure 2. The pressure dependence of the magnetic moment magnitude together with the volume fractions of the three magnetic domains for pressure applied along the *a* axis. The dashed horizontal line denotes the level of equal domain population.
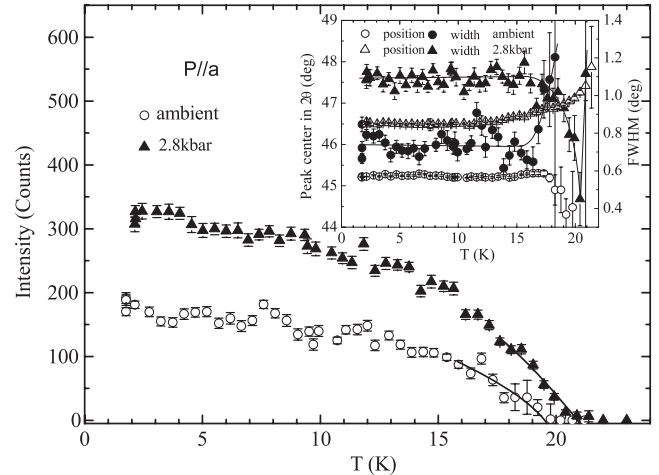

Figure 3. The temperature dependence of the integrated intensity of one of the representative magnetic reflections, which can be indexed within the original hexagonal structure as (1.2 0.9 0.5), measured at ambient pressure and at pressures of 1.9 and 2.8 kbar applied along the *a* axis as a function of temperature. The temperature dependence of the peak position and the full width at half-maximum of this reflection is shown in the inset. Solid lines are guides for the eye.

increasing pressure (by about 0.11 μ_B kbar^{-1}). This would suggest a destruction of the magnetic order in UNiAl at a pressure of about 11.6 kbar. This value is much smaller than the estimate of 105 kbar made on the basis of hydrostatic magnetic studies [9] and electrical resistivity studies [10] that claimed a value of 30 kbar. The description of the observed intensities is fairly good which gives us confidence that the effect of the orthorhombic distortion is not significant.

3.3. The temperature dependence for pressure along the a axis

In figure 3 the integrated intensity of one of the representative reflections measured at ambient pressure and at pressure of 2.8 kbar along the *a* axis as a function of temperature is shown. The temperature dependence of the peak position and the full width at half-maximum is shown in the inset. The reflection which can be indexed within the original hexagonal structure as (1.2 0.9 0.5) disappears at ambient pressure around 19.5 K which is about 0.2 K above the magnetic phase transition temperature as determined from the specific heat [3]. At elevated pressure, however, it persists to higher temperatures. It disappears around 20.5 K and 21.3 K at 1.9 and 2.8 kbar, respectively. The change of the T_N as a function of pressure amounts to about 0.6 K kbar^{-1}. It seems therefore safe to conclude that the application of uniaxial pressure applied perpendicular to the hexagonal axis increases the T_N value. Interestingly, in the vicinity of T_N we encounter different behaviors at ambient and elevated pressures. While under the former conditions the reflection remains at almost the same position for most of the temperature range and just before it disappears moves to lower diffraction angles, at the highest pressure it starts to change its position just above 10 K. Besides that, it shifts to higher diffraction angle, suggesting either further rotation of the propagation vector or increase in its absolute length. The temperature dependences of the width are also different for the two conditions. While at ambient conditions the width remains nearly constant up to T_N and then increases strongly marking the loss of the coherence,

at 2.8 kbar the reflection, before it gets broader above T_N, first gets much narrower. We attribute this observation to inhomogeneous strain existing in the sample.

4. Discussion

Although technically challenging, single-crystal neutron diffraction at low temperatures using uniaxial pressure offers novel insights into various materials. The uniaxial pressure, in contrast to the hydrostatic one, affects the magnetic interactions predominantly along one direction, leaving the others either unaltered or affecting them in the opposite way. As a direct consequence, it is one of the few methods that can reveal the domain population and allow one to decide whether the magnetic structure is of single-*k* or multiple-*k* type. The results presented prove beyond any doubt that the magnetic structure in UNiAl can be described as being composed from three 1 K domains. Moreover, it is shown that the propagation vectors in (still) existing domains under pressure applied along the *a* axis change with pressure in length and direction. This means that the coupling direction is continuously changing with pressure in the real space—an observation that is highly unusual. To the best of our knowledge, all the literature sources describe merely a redistribution of domains or volumes belonging to magnetic structures described using equivalent but different (mainly commensurate) propagation vectors. Among the systems studied by using the neutron diffraction technique under uniaxial pressure in recent times there belong for instance the geometrically frustrated systems $Tb_2Ti_2O_7$ [17] and $ZnCr_2O_4$ [18] and the heavy fermion system $CePd_2Si_2$ [19].

From the field dependence of the propagation vectors at elevated magnetic fields applied along the hexagonal axis it seems that the interaction strengths along various directions

within the basal plane do not differ substantially and one can switch between them rather easily. In a narrow temperature and field range two AF phases seem to be coexisting and stable on the timescale of at least tens of minutes [6]. To the best of our knowledge, it is almost thirteen years since the electronic structure of UNiAl has been calculated in detail [20]. These calculations show, in agreement with photoemission data [21], that the 5f–d hybridization in UNiAl is substantial but with respect to that of nonmagnetic UCoAl considerably reduced. Existing *ab initio* calculations for similar UTX compounds suggest that the application of hydrostatic pressure leads to a smaller unit cell volume causing a stronger overlap between the 5f electron waves and their larger hybridization with other (ligand) states in the solid. Whether it strengthens or weakens in a low-pressure limit, the magnetic exchange interactions depends on the mutual position of the 5f band with respect to the Fermi level and the pressure dependence of the density of states at the Fermi level. Experimentally, the magnetic moment magnitudes seem to decrease by a few per cent upon application of hydrostatic pressure of 4.9 kbar [8]. In any case, hydrostatic pressure does not affect the symmetry [8] and thus it does not alter the exchange competition that is responsible for the occurrence of two different antiferromagnetic phases. In contrast to the application of hydrostatic pressure, that of uniaxial pressure perpendicular to the c axis apparently strengthens exchange along the direction of the applied pressure and thus unbalances the nearly equal exchange paths that existed at ambient pressure. This is manifested especially by the increase of the magnetic phase transition by about 0.6 K kbar^{-1}. This should be compared with the decreases of the same parameter of 0.185 K kbar^{-1} in hydrostatic pressure [8]. Unfortunately, we have not performed a temperature dependence measurement for the pressure applied along the c axis. New, *ab initio* theoretical calculations regarding the stability of various magnetic structures in UNiAl would be highly desirable.

5. Conclusions

In the work presented, the influence of the uniaxial pressure on the crystal structure and the magnetic ordering in UNiAl is presented. It can be stated that the effect of the uniaxial strain applied along the c axis and the a axis is very anisotropic. While the application of a pressure estimated to be few kilobars along the hexagonal axis does not alter the crystallographic structure and merely causes a decrease of the extinction and a small redistribution of magnetic domains, the magnitude of U magnetic moments remains within the error bars constant. For the pressure applied along the a axis, besides a decrease of the extinction, a small distortion of the hexagonal structure has been also detected. A significant redistribution of the magnetic domains and a decrease of the U magnetic moment magnitude by about 0.11 μ_B kbar^{-1} has been observed. The remaining two magnetic domains can no longer be described using ambient pressure propagation vectors. They increase in their length and rotate in the reciprocal space suggesting a shortening and rotation of the modulation wave in real space.

It has been found that the magnetic phase transition temperature increases with the pressure applied along the a axis by about 0.6 K kbar^{-1}. Results for the a axis orientation are in strong contrast to the results obtained previously under hydrostatic pressure conditions.

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