

## PRESSURE-INDUCED PHENOMENA IN U INTERMETALLICS\*

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*(Received July 10, 2002)*

We review experiments devoted to the pressure influence on magnetism in uranium intermetallics, represented by several hexagonal UTX compounds (T = transition metal, X = *p*-metal) and by the tetragonal compound UNi<sub>2</sub>Si<sub>2</sub>. The typical pressure induced phenomena involving the stability of U magnetic moments and their exchange coupling are discussed in conjunction with expected variations of the 5*f*-ligand hybridization.

PACS numbers: 75.30.-m, 71.20.Lp, 75.80.+q

### 1. Introduction

Physics of U intermetallics is intimately connected with the character of the U 5*f*-electron states, which appear at various stages between the localized and itinerant limits depending on the interactions with electrons of ligands of the U atom. Various aspects of electronic structure and magnetism can be tested by studying pressure effects on material parameters. Pressure experiments have recently produced a number of striking results, *e.g.* the pressure-induced enhancement of the tiny U moment in URu<sub>2</sub>Si<sub>2</sub> [1] or the appearance of superconductivity in the ferromagnetic UGe<sub>2</sub> [2], which give to condensed matter research a new momentum.

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\* Presented at the International Conference on Strongly Correlated Electron Systems, (SCES 02), Cracow, Poland, July 10–13, 2002.

Apart from these highly attractive cases also some other pressure-induced phenomena in U intermetallics, although less exotic, deserve attention and some are discussed in this paper. Since the anisotropic  $5f$ -orbitals are principally affected in pressure experiments, the intrinsic impact of external pressure on interatomic distances is emphasized, especially for materials with an anisotropic linear compressibility [3]. In this context the combinations of experiments involving hydrostatic pressure and uniaxial stress are very useful.

The main subjects of our discussion are: the collapse of the itinerant  $5f$ -electron ferromagnetism (antiferromagnetism) in UPtAl (UNiAl) under hydrostatic pressure, phenomena induced in the itinerant  $5f$ -electron metamagnet UCoAl by hydrostatic pressure and uniaxial stress, pressure and field induced changes of the antiferromagnetic (AF) ordering in UNiGa and UNi<sub>2</sub>Si<sub>2</sub>.

## 2. UTX compounds

We will focus on UTX compounds (T = transition metal and X =  $p$ -electron element) with the hexagonal ZrNiAl-type structure. This structure is built up of U–T and T–X basal-plane layers alternating along the  $c$ -axis [4]. The U ground-state moment in compounds of this group varies from 0 to  $1.6 \mu_B$  depending on the degree of itinerancy of the U  $5f$  electrons that is mainly determined by the overlap of the  $5f$  wave-functions centered on the neighboring U atoms and by the  $5f$ -ligand hybridization [4, 5]. All these materials, irrespective of the ground state, exhibit a strong uniaxial magnetic anisotropy [6] as a consequence of the  $5f$ -electron bonding within the basal plane and existence of an orbital  $5f$  magnetic moment. The characteristic magnetic response is observed along the  $c$ -axis whereas the basal-plane directions exhibit Pauli paramagnetism.

### 3. Collapse of ferromagnetism in UPtAl under hydrostatic pressure

UPtAl exhibits ferromagnetic ordering of U moments at  $T_C = 42.5$  K, which is accompanied by a clear anomaly of electrical resistivity and by a spontaneous magnetostriction reaching at low temperatures  $-3 \times 10^{-4}$  and  $2 \times 10^{-4}$  in the basal plane ( $\lambda_a$ ) and along the  $c$ -axis ( $\lambda_c$ ), respectively. In hydrostatic pressures  $p \leq 0.8$  GPa the spontaneous moment is reduced at a rate  $dM_s/dp = -0.027 \mu_B \cdot \text{GPa}^{-1}$  while  $T_C$  increases:  $dT_C/dp = 2.5$  K  $\cdot \text{GPa}^{-1}$  [7]. For higher pressures the  $dT_C/dp$  values become gradually reduced and between 4 and 6 GPa a maximum is seen in the  $T_C$  vs.  $p$  plot (see Fig. 1) followed by a rapid decrease with further increasing pressure [8].

This result is reminiscent of the observations on USe and UTe [9] and it may be conceived with a scenario that considers the dual role of the  $5f$ -ligand hybridization: causing the delocalization of  $5f$  electrons (and the consequent washout of the U magnetic moment) and mediating the exchange interactions between magnetic U sites. The hybridization is usually enhanced with increasing pressure due to reduced interatomic distances and the consequent more extended overlaps of wave functions between neighboring atoms in the lattice. When the hydrostatic pressure is increased, the enhancement of the  $5f$ -ligand hybridization causes a gradual washout of U moment and the consequent suppression of ordered magnetism. On the other hand, the increased overlaps yield an enhancement of exchange integrals that can cause an increase of  $T_C$  with pressure in a limited pressure interval until the U moment is stable. In higher pressures, however, the effect of the ceasing U magnetic moment dominates and the magnetic ordering finally disappears.

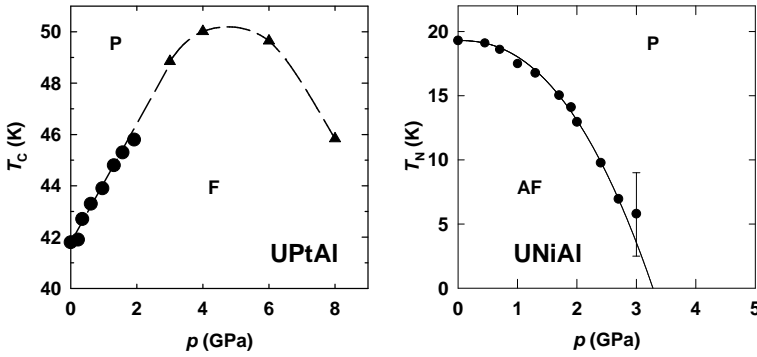


Fig. 1. Pressure dependence of the Curie temperature of UPtAl (left) [8] and the Néel temperature of UNiAl (right); the dashed line is a guide for the eye.

#### 4. Collapse of itinerant $5f$ -electron antiferromagnetism in UNiAl

UNiAl is an itinerant  $5f$ -electron antiferromagnet with spin fluctuations phenomena. The reduced U moments in UNiAl order below  $T_N=19.3$  K in a peculiar AF structure with  $\mathbf{q} = (0.1,0.1,0.5)$  [4, 10]. The AF ordering is destroyed by a magnetic field  $B > B_c$  ( $\approx 11.35$  T below 4 K) applied along the  $c$ -axis [4]. When applying a hydrostatic pressure, the  $T_N$  is initially decreasing at a nearly constant  $dT_N/dp \approx -1.6$  K  $\text{GPa}^{-1}$ . A linear extrapolation to higher pressures points to a critical pressure for the suppression of the AF ordering  $p_c \approx 10$  GPa, provided the  $dT_N/dp$  value remains constant. The  $T_N$  vs.  $p$  dependence (Fig. 1), however, becomes strongly non-linear for  $p > 1$  GPa and  $T_N$  vanishes around 3 GPa [11]. The observed low stability of AF ordering in UNiAl with respect to pressure is one of the principal

attributes of the itinerant  $5f$ -electron antiferromagnetism. In contrast to UNiAl, the isostructural compound UNiGa with a stable local U  $5f$ -moment has  $p_c > 30$  GPa [12]. The U moments in UNiAl are considerably suppressed by pressure [13], whereas the moments in UNiGa are pressure invariant at least up to 0.9 GPa [12] and only moderately reduced in 2.3 GPa [14].

## 5. Pressure induced phenomena in UCoAl

UCoAl exhibits a paramagnetic ground state although the susceptibility has a maximum around  $T_{\max} \approx 20$  K [15]. The magnetic-field induced ferromagnetism at low temperatures qualifies UCoAl as an itinerant electron metamagnet alike YCo<sub>2</sub> [16]. In contrast to the itinerant  $3d$ -electron metamagnets that show the metamagnetic state in rather high magnetic fields (above 70 T in YCo<sub>2</sub>) irrespective to the field direction, the critical field  $B_c$  of the metamagnetic transition in UCoAl is as low as 0.6 T, but should be applied along  $c$ . The metamagnetic transition is accompanied by a magnetostriction effect  $1 \times 10^{-4}$  [17], which is negative along the  $c$ -axis and positive in the basal plane.

A ferromagnetism can be induced in UCoAl by substituting U by small amounts of Y [18] or Lu for U, Fe or Ru for Co [19,20], and Ga, [11] In or Sn for Al [4], but can be suppressed back to the UCoAl-metamagnetism by applying hydrostatic pressure [4,22]. The hydrostatic pressure also causes an increase of  $B_c$  and a suppression of the magnetization step  $M$  across the metamagnetic transition in UCoAl itself. The estimated critical pressure for the disappearance of metamagnetism in UCoAl is 7 GPa [15]. In case of UCoAl also the influence of uniaxial stress along the  $c$ -axis on magnetism in UCoAl was studied [23]. Contrary to the impact of hydrostatic pressure the application of uniaxial stress along the  $c$ -axis of UCoAl leads to a gradual decrease of  $B_c$  yielding a net spontaneous magnetization for  $p > 0.05$  GPa [23] (see Fig. 2).

For physics of UCoAl the anisotropy of the linear compressibility is important. At room temperature  $\partial \ln a / \partial p = 4.2 \times 10^{-3}$  GPa<sup>-1</sup> and  $\partial \ln c / \partial p = 1.1 \times 10^{-3}$  GPa<sup>-1</sup> [3]. Application of hydrostatic pressure causes a considerable enhancement of the  $5f$ - $3d$  hybridization within the basal plane yielding a delocalization of  $5f$ -electron states. Consequently, the  $B_c$ -value increases similar to the behavior of the archetypal itinerant electron metamagnets like YCo<sub>2</sub> [16]. This mechanism probably dominates the effects of shrinking the  $c$ -axis. The uniaxial stress along the  $c$ -axis causes shrinking interatomic distances along  $c$  and expansion within the basal plane. The consequent reduced  $5f$ - $3d$  hybridization within the basal plane may be stabilizing the U moment. This scenario is plausible also in the light of magnetostriction data in UCoAl across the metamagnetic transition that is accompanied by

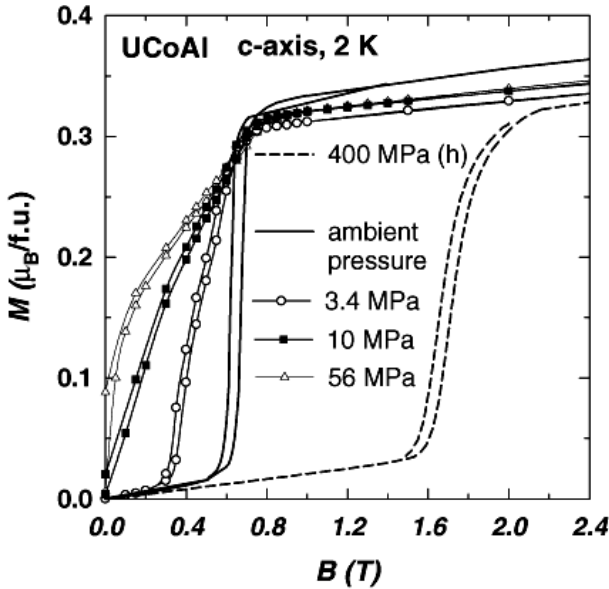


Fig. 2. Magnetization curves measured in magnetic field along the  $c$ -axis on a single crystal of UCoAl exerted to various values of uniaxial stress. The magnetization curve obtained at ambient pressure illustrated by a full bold line and the dashed line that represents data for a hydrostatic pressure of 400 MPa are given for comparison [23].

shrinkage of the  $c$ -axis and expansion of the  $a$ -axis [17]. This implies that the ferromagnetic state in UCoAl can be stabilized by application of the uniaxial stress along the  $c$ -axis leading to the expansion of the  $a$ -axis.

## 6. Pressure-induced changes of magnetic propagation in UNiGa

In UNiGa several types of AF structures are observed below 40 K [4,24]. The onset of an AF ordering is characterized by an incommensurate AF structure (ICAF) with a wave vector  $\mathbf{q} \approx (0,0,0.36)$ . At 37.3 K, a first-order transition is observed to a commensurate AF structure with a periodicity  $3c$  (AF-3c). With further decreasing temperature, UNiGa undergoes gradual transformation to the ground-state AF phase (AF-6c) with the  $++-+-$  stacking via the “intermediate”  $++-+-$  phase (AF-8c). All these AF phases are built of basal-plane ferromagnetic sheets of U moments oriented along the  $c$ -axis and differ in the moment stacking along the  $c$ -axis. The simple AF phase  $+-$  stacking (AF-2c) is absent in ambient pressure. The U moment ( $\sim 1.4 \mu_B$  at 2 K) does not decrease substantially with increasing temperature almost up to 35 K, where they retain more than 90 %

of their low-temperature value. The combination of a relatively high Néel temperature (40 K), a very small magnetic field of the metamagnetic transition ( $< 1.5$  T) and the collection of long-period AF structures depending on temperature indicates that physics of UNiGa is connected with a delicate balance of ferromagnetic and AF exchange interactions. To understand the special hierarchy of exchange interactions in UNiGa, the influence of external pressure that modifies interatomic distances is of an obvious interest. The evolution of magnetic phases in UNiGa with pressure is seen in the  $p$ - $T$  magnetic phase diagram (Fig. 3), which has been constructed from results of several pressure experiments on UNiGa [12, 25, 26].

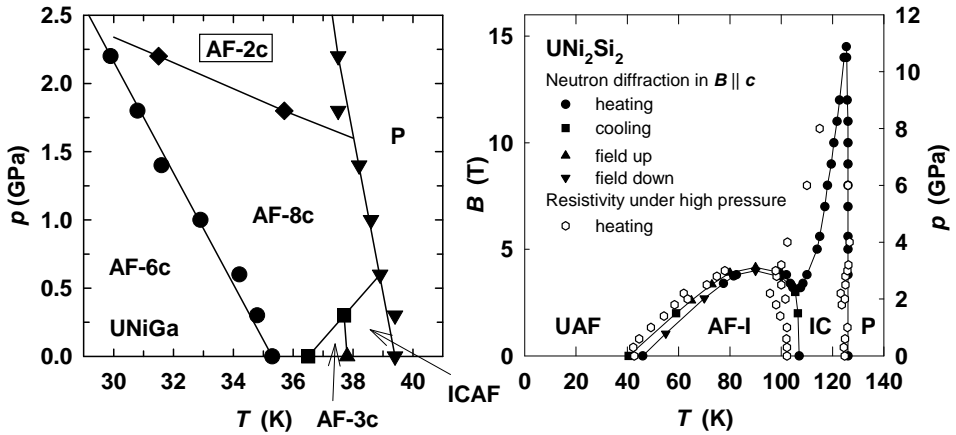


Fig. 3. The  $p$ - $T$  phase diagram of UNiGa (left) [14] and the combined  $B$ - $T$  and  $p$ - $T$  magnetic phase diagrams of UNi<sub>2</sub>Si<sub>2</sub> [27].

The ICAF phase is suppressed already by 0.3 GPa, the AF-3c phase ceases in pressures above 0.6 GPa. Only the AF-6c and AF-8c phases remain in higher pressures and the temperature range of the latter phase becomes gradually extended with increasing pressure on account of the ground state phase. In pressures  $p \geq 1.8$  GPa a new magnetic phase is induced to replace the phase AF-8c. The U magnetic moment remains intact in pressures up to 0.9 GPa. The neutron diffraction experiment up to 2.3 GPa [14] confirmed that the “new” high-pressure induced phase is characterized by the simple  $+ -$  AF stacking (we denote it as **AF-2c**). This conclusion is consistent with the previously reported pressure effects on values of the field of metamagnetic transitions that point to enhancement of AF exchange interactions [12]. An uniaxial-stress experiment is desirable to address different components of the strongly anisotropic exchange interactions (ferromagnetic within the basal plane and predominantly AF along the  $c$ -axis) in UNiGa.

## 7. Suppression of simple antiferromagnetism in UNi<sub>2</sub>Si<sub>2</sub> under magnetic fields and hydrostatic pressures

UNi<sub>2</sub>Si<sub>2</sub> crystallizes in the body-centered tetragonal ThCr<sub>2</sub>Si<sub>2</sub>-type of structure (space group I4/mmm) [4] and orders magnetically below  $T_N = 124$  K with an incommensurate (IC) modulation of U magnetic moments along the  $c$ -axis. The IC phase is characterized by a propagation vector  $\mathbf{q} \approx (0, 0, 0.745)$ . Upon cooling across  $T_2 = 103$  K, UNi<sub>2</sub>Si<sub>2</sub> undergoes a first-order magnetic phase transition from the IC phase to a body-centered AF-I structure. At temperatures below 53 K, another order-to-order magnetic phase transition to the uncompensated AF (UAF) ground-state phase with  $\mathbf{q} = (0, 0, 2/3)$  takes place. The ordered phases exhibit all the basal-plane ferromagnetic sheets of the U moments oriented along the  $c$ -axis and differ mainly in the moment stacking along the  $c$ -axis. In particular, the AF-I phase is characterized by  $+-$  coupling and the UAF phase by  $++-$  coupling of equal U moments. The U moments in the IC phase are supposed to be sinusoidal modulated along  $c$  [28,29].

Application of the field along the  $c$ -axis yields a strong increase of  $T_1$ , *i.e.* an extension of the stability range of the low-temperature phase (UAF) at the expense of the AF-I phase (see the magnetic phase diagrams in Fig. 3) [28,30]. The high-temperature boundary of the AF-I phase is initially almost field independent. Above 3 T, however, it becomes gradually reduced. As a consequence, the interval of the stability of AF-I phase shrinks rapidly with increasing field and the AF-I phase is fully suppressed in fields above 4.4 T. On the other hand,  $T_N$  is practically invariable up to 14.5 T [28]. As can be seen in Fig. 3, the application of hydrostatic-pressure has an analogous influence on the magnetic phases in UNi<sub>2</sub>Si<sub>2</sub>, like magnetic field. The AF-I phase is suppressed at pressures above 3.4 GPa [31]. A possible explanation of this pressure evolution can be given within the Ising model with the third-neighbor interaction included (A3NNI model) [32].

## 8. Concluding remarks

Several case studies of the influence of external hydrostatic pressure and uniaxial stress on magnetism in uranium intermetallics were discussed. For UPtAl, UNiAl and UCoAl, application of hydrostatic pressure yields a much stronger compression of the basal plane (due the much stronger compressibility of the basal plane). This leads to a strong overlap of  $5f$  (U) and  $5d$  (Pt) or  $3d$  (Ni,Co) wave-functions and a consequent delocalization of  $5f$ -electron states. Then in UPtAl and UNiAl one can expect that the principal pressure impact is realized on the U moment while the enhancement of the exchange integral plays only a side role. Since the U magnetic moment is composed of the mutually compensating orbital and spin components, the negative pressure effect on the orbital component, while the spin part may be affected by

pressure only very little, will produce a strongly non-linear pressure dependence of U moment. Consequently, for UNiAl with a much more delocalized  $5f$  moment the value of  $T_N$  decreases already in lowest pressures. The rate of decrease of  $T_N$  with pressure becomes gradually enhanced and the antiferromagnetism in UNiAl collapses at a much lower pressure than estimated by linear extrapolation from low-pressure regime. In UPtAl, which is characterized by a considerably larger value of U moment in ambient pressure, the pressure-induced enhancement of exchange integral presumably dominates the situation at lower pressures where the  $T_C$  increases. Above 4 GPa, however, the negative pressure effect on the U moment probably takes over and the  $T_C$ -value finally starts to decrease as a precursor of a collapse of ferromagnetism in pressures above 8 GPa.

The effects on the itinerant  $5f$ -electron metamagnet UCoAl induced by the hydrostatic pressure and uniaxial stress can be conceived with the scenario considering the principal role of modifications of interatomic distances within the basal plane on the delocalization of  $5f$ -electron states, which is critical for the conditions for appearance of metamagnetism. How far the pressure effects influence the delicate balance of AF and ferromagnetic exchange interactions one cannot conclude at this stage of research.

The U sites in UNiGa and UNi<sub>2</sub>Si<sub>2</sub> are characterized by a weak  $5f$ -ligand hybridization and a large local U moments that is clearly demonstrated by almost pressure independent Néel temperature. Variations of interatomic distances induced by the applied pressure seem to have a negligible effect also on the size of U magnetic moment. On the other hand, the pressure-induced transitions from one magnetic structure to another clearly manifest the changes in the hierarchy of exchange-interaction component.

This work is a part of the research program MSM113200002 that is financed by the Ministry of Education of the Czech Republic. It has been also supported by the Grant Agency of the Czech Republic (grant # 202/02/0739).

## REFERENCES

- [1] H. Amitsuka, M. Sato, N. Metoki, M. Yokoyama, K. Kuwahara, T. Sakakibara, H. Morimoto, S. Kawarazaki, Y. Miyako, J.A. Mydosh, *Phys. Rev. Lett.* **83**, 5114 (1999).
- [2] S.S. Saxena, P. Agarwal, K. Ahilan, F.M. Grosche, R.K.W. Haselwimmer, M.J. Steiner, E. Pugh, I.R. Walker, S.R. Julian, P. Monthoux, G.G. Lonzarich, A. Huxley, I. Sheikin, D. Braithwaite, J. Flouquet, *Nature* **406**, 587 (2000).
- [3] L. Havela, M. Diviš, V. Sechovský, A.V. Andreev, F. Honda, G. Oomi, Y.H.S. Méresse, *J. Alloy. Compd.* **322**, 7 (2001).



- [4] V. Sechovský, L. Havela, *Handbook of Magnetic Materials*, Elsevier, Amsterdam 1998, **11**, p.1.
- [5] D.D. Koelling, B.D. Dunlap, G.W. Crabtree, *Phys. Rev.* **B31**, 4966 (1985).
- [6] V. Sechovský, L. Havela, F.R. de Boer, E. Brück, *J. Alloy. Compd.* **181**, 179 (1992).
- [7] A.V. Andreev, J. Kamarad, F. Honda, G. Oomi, V. Sechovský, Y. Shiokawa, *J. Alloy. Compd.* **314**, 51 (2001).
- [8] F. Honda, T. Eto, G. Oomi, A.V. Andreev, V. Sechovský, N. Takeshita, N. Mori, *High Pressure Research* **22**, 159 (2002).
- [9] P. Link, U. Benedict, J. Wittig, H. Wuhl, *Physica B* **190**, 68 (1993).
- [10] K. Prokeš, F. Bourdarot, P. Burlet, P. Javorský, M. Olsovec, V. Sechovský, E. Brück, F.R. de Boer, A.A. Menovsky, *Phys. Rev.* **B58**, 2692 (1998).
- [11] O. Mikulina, J. Kamarád, A. Lacerda, O. Syshchenko, T. Fujita, K. Prokeš, V. Sechovský, H. Nakotte, W.P. Beyermann, *J. Appl. Phys.* **87**, 5152 (2001).
- [12] F. Honda, K. Prokeš, M. Olsovec, F. Bourdarot, P. Burlet, T. Kagayama, G. Oomi, L. Havela, V. Sechovský, A.V. Andreev, E. Brück, F.R. de Boer, A.A. Menovsky and M. Mihalik, *J. Alloys and Compounds* **271-273**, 495 (1998).
- [13] K. Prokeš, T. Fujita, N.V. Mushnikov, S. Hane, T. Tomita, T. Goto, V. Sechovský, A.V. Andreev, A.A. Menovsky, *Phys. Rev.* **B59**, 8720 (1999).
- [14] V. Sechovský, K. Prokeš, F. Honda, B. Ouladdiaf, J. Kulda, *Appl. Phys. A* (2002), in press.
- [15] N.V. Mushnikov, T. Goto, K. Kamishima, H. Yamada, A.V. Andreev, Y. Shiokawa, A. Iwao, V. Sechovský, *Phys. Rev.* **B59**, 6877 (1999).
- [16] T. Goto, H.A. Katori, T. Sakakibara, H. Mitamura, K. Fukamichi, K. Murata, *J. Appl. Phys.* **76**, 6682 (1994).
- [17] A.V. Andreev, R.Z. Levitin, Yu.F. Popov, R.Yu. Yumaguzhin, *Sov. Phys. Solid State* **27**, 1145 (1985).
- [18] A.V. Andreev, I.K. Kozlovskaya, N.V. Mushnikov, T. Goto, V. Sechovský, L. Havela, Y. Homma, Y. Shiokawa, *J. Magn. Magn. Mater.* **197**, 658 (1999).
- [19] A.V. Andreev, V. Sechovský, D. Rafaja, L. Dobiasova, Y. Homma, Y. Shiokawa, *J. Alloy. Compd.* **307**, 77 (2000).
- [20] A.V. Andreev, H. Aruga Katori, T. Goto, *J. Alloy. Compd.* **224**, 117 (1995).
- [21] A.V. Andreev, N.V. Mushnikov, T. Goto, V. Sechovský, *Phys. Rev.* **B60**, 1122 (1999).
- [22] A.V. Andreev, L. Havela, V. Sechovský, M.I. Bartashevich, T. Goto, K. Kamishima, *Physica B* **239**, 88 (1997).
- [23] V. Sechovský, A.V. Andreev, Y. Ishii, M. Kosaka, Y. Uwatoko, *High Pressure Research* **22**, 155 (2002).
- [24] K. Prokeš, E. Brück, F.R. de Boer, M. Mihalik, A.A. Menovsky, P. Burlet, J.M. Mignot, L. Havela, V. Sechovský, *J. Appl. Phys.* **79**, 6396 (1996).
- [25] Y. Uwatoko, G. Oomi, V. Sechovský, L. Havela, E. Brück, F.R. de Boer, *J. Alloy. Compd.* **213-214**, 281 (1994).

- [26] V. Sechovský, L. Havela, F.R. de Boer, E. Brück, Y. Uwatoko, G. Oomi, *Physica B* **186-188**, 697 (1993).
- [27] F. Honda, G. Oomi, P. Svoboda, A. Syshchenko, V. Sechovský, S. Khmelevski, M. Diviš, A.V. Andreev, N. Takeshita, N. Mori, A.A. Menovsky, *J. Magn. Magn. Mater.* **226-230**, 585 (2001).
- [28] P. Svoboda, P. Javorsky, V. Sechovský, A.A. Menovsky, *Physica B* **276-278**, 686 (2000).
- [29] L. Rebelsky, H. Lin, M.W. McElfresh, M.F. Collins, J.D. Garrett, W.J.L. Buyers, M.S. Torikachvili, *Physica B* **180-181**, 43 (1992).
- [30] A. Syshchenko, V. Sechovský, A.V. Andreev, R.V. Dremov, J. Šebek, A.A. Menovsky, *J. Appl. Phys.* **85**, 4554 (1999).
- [31] F. Honda, M. Matsuda, G. Oomi, N. Mori, N. Takeshita, V. Sechovský, A.V. Andreev, A.A. Menovsky, *Phys. Rev. B* **61**, 11267 (2000).
- [32] Y. Muraoka, *Phys. Rev.* **B64**, 134416 (2001).