Physics of the f-Electron Intermetallics

© *Wojciech Suski*

W. Trzebiatowski Institute of Low Temperature and Structure Research of Polish Academy of Sciences,
P.O. Box 1410, PL–50–950 Wroclaw 2, Poland
International Laboratory of High Magnetic Fields and Low Temperatures,
PL–53–421 Wroclaw, Poland

Properties of lanthanide and actinide intermetallics are extremely interesting from the point of view of both application and fundamental research. The impact on starting fundamental research on the f-electron materials undoubtlessy were the determination of the ferromagnetic properties of UH_3 and UD_3 by the research group of the present Institute of Low Temperature and Structure Research in Wroclaw and detection of the mixed valence state in samarium monochalcogenides at A.F. Ioffe Physicotechnical Institute in Leningrad (at that time). Since that time the phenomena of the mixed valence, heavy fermion state as well as complicated magnetic structures have been under intensive investigation in numerous laboratories all over the world. As the examples, the exotic magnetic structures of $CeSb$ and UNi_4B are described. Then the problems of the heavy fermion state existing in UBe_{13} and $UCu_{4+x}Al_{8-x}$ are presented. Next, the non-Fermi-liquid behavior appearing due to magnetic instability is discussed. Finally, some perspective for further research is proposed.

Solid State Physics is strongly attached to materials. The examples of materials which have recently been broadly investigated in many solid state laboratories are those containing the lanthanide and, to a lesser extent, the actinide elements. Lanthanides and actinides are the representatives of two families that develop the f-electron shell (however, heavier actinides are only artifically obtained) and are radioactive. The physical properties of these two groups of elements and their compounds deserve a vast interest because of their intriguing fundamental properties resulting from the electronic structure and broad application. This last reason concerns obviously only lanthanides.

The properties of actinides became known after the results of the Manhattan Project got clearance, but the broad interest started as soon as pecularities of the actinide electronic structure were apparent.

The investigations into the physical properties of the lanthanide intermetallics started about four decades ago when separated lanthanide elements became available and reasonable good samples were succesfully prepared (at first polycrystals and latter single crystals).

As magnetic studies proceeded, it was soon found out that a plentitude of magnetic behavior was materialised in these intermetallics, which in many instances were observed nowhere else. Therefore it is no wonder that one of the most important applications of the $4f$-electron materials is their use as hard magnetic materials. Another promising direction is a vast field of high temperature superconductivity.

1. Electronic Structure

As mentioned above both lanthanides and actinides are families of the elements which develop the f-electron shell.

However, there are the striking differences between the individual representatives of these families depending on the degree of localization of the f-electrons resulting from their location in relation to the Fermi level, to the band states and to the spatial extension of the f-shell. In the majority of lanthanides and heavier actinides the f-electrons are localized, located below the Fermi level and protected from the influence of surrounding and external factors. They exhibit localized magnetic moments with value which is close to that of the free ion. These elements exhibit also magnetic order. However, light actinides and some lanthanides which have electronic configurations close to the particularly stable ones: f^0, f^7 and f^{14} exhibit different behavior. The f-level is located fairly close in energy to the valence and bonding electrons, and to the Fermi level. As the result, the f-electrons contribute to the conduction process along with the d and s-electrons and hybridize with them strongly. The spatially extended f-shell is extremely sensitive to any influence of the external factors such as pressure and magnetic and crystal fields. Therefore, different interactions, existing in the f-electron ion in a delicate balance, are the reason for the unusual properties and examples of some of them will be described below, e.g., the strong hybridization, huge magnetocrystalline anisotropy, complex magnetic ordering, spin-fluctuation, heavy fermion, Kondo lattice, mixed valence, etc., when the f-electron elements form the compounds.

2. Anomalus lanthanides and Actinides

The celebration of the Ioffe Institute Anniversary is a good occasion to remind that the initiation of the fundamental research on the f-electron materials has came from the Jubilee Institute as well as from the team in which the present speaker has spent all his scientific life. It is strange enough that the first experiments have concerned the actinides. In the late forties, W. Trzebiatowski and his co-workers, examining the magnetic properties of the uranium hydride and deuteride for determination of the uranium electronic structure in these compounds, discovered ferro-magnetism in both compounds below $\sim 180\,K$ (for detailed references see [1]). The authors hesitated for a long time to publish unexpected results up to 1952 but then this fact got
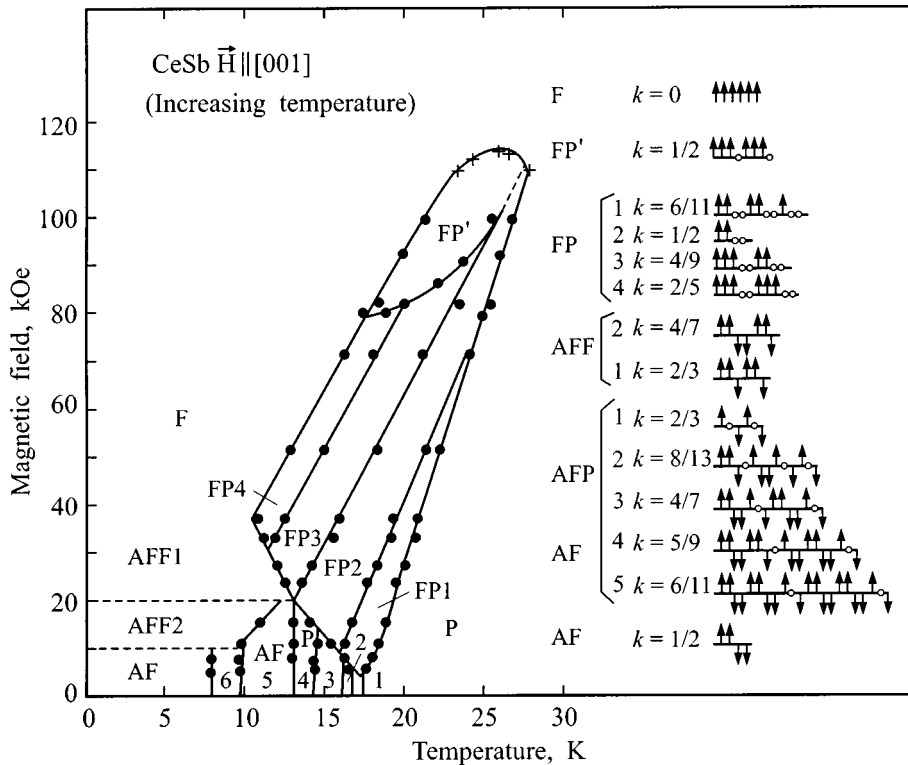
**Figure 1.** Magnetic (H, T) phase diagram for CeSb [8].

confirmation in other laboratories (see [1]). The electronic structure of the uranium in semi- or intermetallic compounds is still a puzzle but magnetic ordering has been discovered in numerous compounds of uranium and other actinides [2–4]. Now all types of magnetic ordering and coherent states have been found in these compounds. Available space does not permit to discuss this problem in detail but some examples will be presented below.

The other phenomenon — mixed valence state — was discovered in Ioffe Institute in the sixties when the change of the colour of magnetic semiconductors — monochalcogenides of samarium — was observed after applying a small stress. It was also detected that the electrical resistivity of these compounds having cemiconductor character suddenly decreases under pressure showing the transformation to a metallic state. Then this behavior was found in other compounds of Ce, Sm, Eu, Tm and Yb, developing under influence of other factors, not only pressure. The early period of this research is summarized in [5], terminology, the models explaining this phenomenon as well as more recent experimental results are collected in [6] and the most recent experimental results are presented in [7].

Both these groups of phenomena are an indication that the unusual electronic structure of the lanthanides and actinides is the reason for uncommon properties of these materials.

Below, we are going to discuss some examples of this behavior, starting from unusual magnetic structures. Fig. 1 shows the (H, T) phase diagram observed for CeSb [8]

(for other references see [9]). This phase diagram contains the largest number of collinear magnetic phases ever known. It can be noted that there are the 15 distinct phases, 7 of them being successively stabilized in zero field when temperature is decreased, which correspond to long period commensurate structures as it is shown in fig. 1 [8]. The magnetic field creates the ferromagnetic layers and at low temperatures form finally a simple ferromagnetic (F) structure. At higner temperatures, the field destroys antiferromagnetic (AF) layers and rearranges a sequence of paramagnetic layers from single to double ones. Only the ferro-paramagnetic (FP) phase persisting in the highest field contains again simple paramagnetic layers. The most unusual feature of CeSb, however, comes from the coexistence in the so-called antiferro-paramagnetic (AFP) and FP phases in which several regions of magnetic and non- (or para-)magnetic Ce atoms are observed. The inelastic scattering with polarized neutrons giving magnetic excitation spectra have determined the crystal-electric-field (CEF) ground state of magnetic Ce atoms being a Γ_8 quartet with large magnetic moment $(2.1\,\mu_B)$, whereas that of paramagnetic Ce atoms being a Γ_7 doublet with smaller moment $(0.7\,\mu_B)$ [10]. This unusual phase diagram is not yet fully understood but its origin seems to be found in the large anisotropic hybridization between p-holes of Sb and the Γ_8 states of Ce^{3+}. Other concepts, such as sole CEF effects, devil's staircase and ANNNI (anisotropic next nearest neighbors Ising) models have been considered but
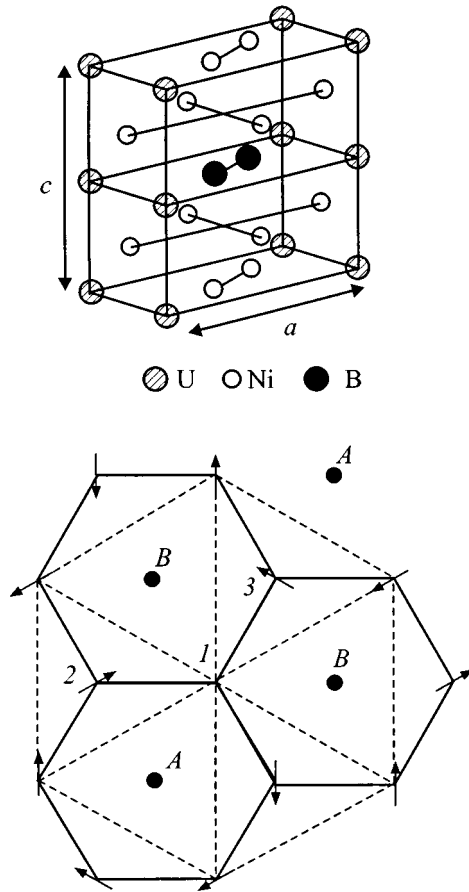
Figure 2. Crystal and magnetic structure of UNi$_4$B. *a* — crystal structure of the CeCo$_4$B-type subcell UNi$_4$B; *b* — zero-field magnetic structure of UNi$_4$B (projection on the basal plane). The arrows show the magnetic moments, while the solid circles represent the Kondo screened U sites (according to [16]). Lattice distortions differentiate *A* and *B* nonmagnetic sites, reducing (increasing) the distance between *1* and *2* (*1* and *3*) magnetic U atoms.

no apprecialbe results have been obtained (for references see [9]). Different approach for explanation of this complex phase diagram has been applied introducing an incommensurate mean field model [11]. In this model, paramagnetism on one part of Ce atoms arises because there is no exchange field at their sites. This phase diagram undergoes also a dramatic change under pressure (for references see [9]). The existence of the paramagnetic (P) phases is actually suppressed above 1 GPa. It is clear that more theoretical investigations are still needed to account for this exceptional behavior.

One of the most unusual magnetic structures has been detected in UNi$_4$B [12–16]. In this crystal structure (hexagonal, CeCo$_4$B-type, $P6/nmm$ space group), presented in fig. 2, *a*, only U atoms have a magnetic moment and they display hexagonal arrangement in the basal plane. The separation of the nearest-neighbor (nn) U atoms in the basal plane is larger than that in the perpendicular direction

($a/0.5c = 1.4$), creating triangular lattice of F chains. This arrangement is certainly related to the geometrical frustration of this triangular lattice with AF interaction. Below 20 K, the neutron diffraction (ND) experiments [12,13] show that only 2/3 of the U moments order AF in a complex structure in which the magnetic unit cell contains nine U atoms as it is shown in fig. 2, *b* [14]. Six ordered magnetic U moments are arranged perpendicularly to the *c* axis forming a 120° angle between the next-nearest-neighbors (nnn). Application of magnetic field along the *c*-axis or parallel to the basal plane reveals strong anisotropy of the system. This magnetic structure has been described [12] as two independent spin systems, of which one orders while the other remains paramagnetic down to low temperatures. It was proposed that 1/3 of the U atoms form chains within the ordered spin matrix that stabilize their one-dimensional character because the local field vanishes on those sites. The expected ordering of these "paramagnetic" sites when a small field is applied is not, however, experimentally confirmed, suggesting another explanation for these 1/3 U atoms behaviour. Lacroix et al. [16] suggest that these 1/3 U atoms are nonmagnetic due to the Kondo effect. They present a model in which the coexistence of magnetic and nonmagnetic U atoms is the consequence of competition between frustration of the crystallographic structure and the instability of 5f-moments.

The heavy fermion (HF) state is one of the most exciting topics of the contemporary solid state physics. At low temperatures, some of the f-electron systems exhibit properties that seem to have switched upon cooling from those of system of local moments to those of a narrow energy band of mobile electrons. These materials sometimes order magnetically, but the ordered magnetic moments are a fraction of the large high temperature f-electron moment. Interest in this problem heightened when it was discovered that one of these compounds, CeCu$_2$Si$_2$, is a superconductor (for references see e.g. [6,17,18]). The large specific heat discontinuity at the superconducting transition shows that the itinerant electrons act as though they have a mass some 100 times larger than that of an electron in a typical metal. The superconducting state often displays unusual properties and complicated phase diagrams involving several superconducting phases. A large number of HF systems are now known. Most of these materials are intermetallic compounds containing Ce or U, whose atoms have incomplete f-shells. A few contain the lanthanide Yb or the actinide Np or Pu as the essential ingredient. It is now well established that the f-electrons on the lanthanide or actinide atoms are responsible for all of the unusual properties, but there is no agreement among the investigators on the mechanism or mechanisms by which f-shell electrons can produce the observed effects.

The cubic actinide compound UBe$_{13}$ has been identified as the second HF conductor by Ott et al. [19] but its magnetic properties have been determined by the team from the author's Institute [20]. Preliminary observation of superconductivity in a UBe$_{13}$ sample [21] has been interpreted as resulting from precipitations of spurious phases in form of

fine filaments. The results concerning UBe_{13} and its solid solutions are collected in [4,6,22]. UBe_{13} does not show the three-dimensional magnetic ordering. Its electrical resistivity, upon cooling, first increases and passes through a maximum at about 30 K. In pure UBe_{13} this maximum is hardly resolvable, as $\rho(T)$ increases again sharply to a second maximum at about 2.5 K [22]. At even lower temperatures, $\rho(T)$ decreases steeply. In the low-temperature range of this decrease, an extraordinarity strong negative magnetoresistivity is observed. At these temperatures, HF behavior occurs with $\gamma = 0.72 - 0.86 \, J/K^2 mol$ (see [22]). UBe_{13} becomes superconducting at about 0.9 K. The properties of UBe_{13} can be influenced dramatically by deliberate doping with an extremely strong influence of substitution on the Be-sites.

The HF state has been also detected in Wroclaw in the $UCu_{4+x}Al_{8-x}$ system which exists for $0 \leqslant x \leqslant 2$ (for review see [23]). The simple AF ordering was determined in the U sublattice by the neutron diffraction (ND) for x not far from $x = 0$ ($T_N(x = 0) \approx 40 \, K$). The electronic specific heat coefficient amounts to about $0.12 \, J/K^2 mol$, however, for $x = 1.5$ the magnetism disappears and γ increases to $0.8 \, J/K^2 mol$, suggesting HF-like behavior. The reason for such a high γ value is a mistery since the material does not transform to the superconducting state at low temperature (for references see [23]). Structural disorder as the reason for both high γ and the absence of magnetic ordering and superconducting state for higher x has been excluded by a recent ND experiment (for references see [23]). It might be that the increase of Cu concentration causes a volume compression, which is not large enough to decrease the U–U separation below the Hill lilmit necessary for the superconducting state for the uranium compounds, but which might result in an enhanced $5f$-ligand hybridization. Then in the spirit of the Doniach [24] phase diagram the $5f$-conduction-electron-exchange coupling is shifted from below to above the critical value at which the AF order vanishes. Further on, the L-absorption-edge-shift experiment [25] shows that the uranium valence depends strongly on stoichiometry (x) and for all x, uranium exhibits nonintegral occupance of the $5f$-shell. This phenomenon results probably from simultaneous existence of the uranium $5f$-electrons in two states: itinerant and localized, with the decrease of the occupance of the $5f$-shell corresponding to the increase of x, the $5f$-shell thus getting closer to the Fermi level. At the same time, the density of states on the Fermi level increases substantially, which is related to the observed increase of γ.

Recently, the transition from heavy Landau Fermi liquid (HLFL) to non-Fermi liquid (NFL) behavior has been observed in numerous U- and Ce-containing systems. HLFL and NFL states can be distinguished by different temperature dependences of magnetic susceptibility, χ, electrical resistivity, ρ, and specific heat, C or C/T. For HLFL: the susceptivility follows the Curie–Weiss law at high temperature and at low temperature exhibits almost temperature independent paramagnetism (Pauli type), $\rho \sim AT^2$ and $C \sim \gamma T$, respectively, and for NFL: $\chi \sim \ln T$
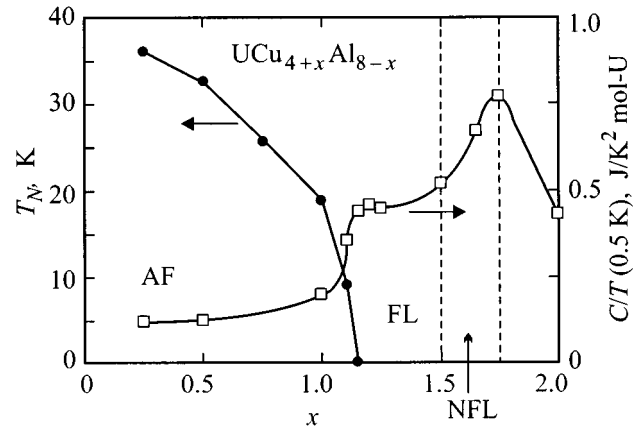
Figure 3. Phase diagram of $UCu_{4+x}Al_{8-x}$ [26]: C/T at 0.5 K (right hand scale, squares).

or $\chi \sim (1 - T^{1/2})$, $\rho \sim T$ and $C \sim -T \ln T$, respectively. Both regimes are separated by the quantum critical point (QCP) but they can also coexist. This state can be induced by a change of composition and also by pressure. The HLFL state can coexist with anti- and ferromagnetic ordering, spin fluctuation (SF) and spin glass state, whereas the NFL state appears in a very narrow compositon range (pressure) in which magnetic instability desappears. Nishioka et al. [26] have presented the phase diagram of $UCu_{4+x}Al_{8-x}$ system for x dependence of C/T at 0.5 K and Néel temperature, derived from the specific heat and magnetic measurements, shown in fig. 3. It is to be seen that in this system three states can exist: AF, HLFL and NFL depending on x. Moreover, Krimmel et al. [27] claim that for $x = 0.75$ the indication of SF is seen. It is clear that the NFL state arises due to very tiny composition change and exists in considerable concentration range. A two-channel Kondo model was proposed to explain the NFL behavior in the uranium compounds. Unfortunatelly, this model turns out to be inadequate to describe NFL behavior in Ce alloys (for reference see e.g. [28]). It was also suggested that the NFL state for many materials, in which this state is artificially induced by alloying or pressure, has a distortion of lattice as the reason for formation. The persistence of NFL behavior over an extended range of concentration and coexistence of Fermi-liquid and non-Fermi-liquid characteristics indicates a complex nature of the low temperature state.

In Summary, most probably, the coming XXI century will be facing further progress in the solid state physics of the f-electron materials. But serious development will be possible only if the three particular problems will find enough support.

1. Development of technology especially of single crystal samples including that of transuranium elements. The basis for that is an improvement of the Czocharalski multi-arc method. Also MBE and laser ablation methods should produce new magnetic and superconducting materials.

2. Further progress in experimental methods, particularly those which applied the nuclear physics methods to solid state physics. Some of them allow to determine local properties. The present author believes that, for example, the magnetic resonance *X*-ray scattering will supply new information concerning electronic structure including the ratio of orbital and spin parts of magnetic moment for light actinides and anormal lanthanides (see e.g. [29]).

3. Development of the theory of multibody interactions and further progress in computational techniques which allow to carry out the complicated band structure calculation.

However, all the presently observed development can be prolonged if society will understand that the progress in the solid state physics means the progress in technology and in industry and for that enough money should be available. Solid state physics is not an extremely expensive research, after all.

References

[1] R. Troć, W. Suski. J. Alloys Compd. **219**, 1 (1995).

[2] J.-M. Fournier, R. Troć. In: Handbook on the Physics and Chemistry of the Actinides. V. II / Ed. by J.A. Freeman and G.H. Lander. Elsevier, N.-Y., (1985). P. 29.

[3] V. Sechovsky, L. Havela. In: Handbook of Magnetic Materials. V. 4 / Ed. by E.P. Wohlfarth and K.H.J. Buschow. Elsevier, Amsterdam (1988). P. 310.

[4] W. Suski, R. Troć. In: Landolt–Börnstein Numerical Data and Functional Relationships in Science and Technology. New Series / Ed. by W. Martienssen. Group III: Solid State Physics, vol. 19, subvol. f2: Actinide Elements and Their Compounds with Other Elements. Part 2 / Ed. by H.P.J. Wijn (Springer, Berlin (1993). P. 1.

[5] I.A. Smirnov, V.S. Oskotskiĭ. Usp. Fiz. Nauk **124**, 241 (1978).

[6] P. Wachter. In: Handbook on the Physics and Chemistry of Rare Earths. V. 19 / Ed. by K.A. Gschneidner, Jr., L. Eyring, G.H. Lander, and G.R. Choppin. North–Holland, Amsterdam (1993). P. 1.

[7] T. Palewski, W. Suski. In: Landolt–Börnstein Numerical Data and Functional Relationships in Science and Technology. New Series / Ed. by W. Martienssen. Group III: Condensed Matter, vol. 27: Magnetic Properties of Non-Metallic Inorganic Compounds Based on Transition Elements, subvol. C1: Binary Lanthanide Oxides / Ed. by H.P.J. Wijn, Springer, Berlin (1997). P. 1; *ibid.*, Binary Lanthanide Chalcogenides / Ed. by H.P.J. Wijn. Springer, Berlin (1998), in press.

[8] J. Rossat-Mignod, P. Burlet, L.P. Regnault, C. Vettier. J. Magn. Magn. Mater. **90/91**, 5 (1990).

[9] T. Palewski, W. Suski. In: Landolt–Börnstein Numerical Data and Functional Relationships in Science and Technology. New Series / Ed. by W. Martienssen. Group III: Condensed Matter, vol. 27: Magnetic Properties of Non-Metallic Inorganic Compounds Based on Transition Elements, subvol. B1: Binary Lanthanide Pnictides / Ed. by H.P.J. Wijn. Springer, Berlin (1998). P. 1.

[10] L.P. Regnault, J.L. Jacoud, C. Vettier, T. Chattopadhyay, J. Rossat-Mignod, T. Suzuki, T. Kasuya, O. Vogt. Physica **B156/157**, 798 (1989).

[11] M. Date. J. Phys. Soc. Jpn. **57**, 3682 (1988).

[12] S.A.M. Mentink, A. Drost, G.J. Nieuwenhuys, E. Frikkee, A.A. Menovsky, J.A. Mydosh. Phys. Rev. Lett. **73**, 1031 (1994).

[13] S.A.M. Mentink, G.J. Nieuwenhuys, H. Nakotte, A.A. Menovsky, A. Drost, E. Frikkee, J.A. Mydosh. Phys. Rev. **B51**, 11 567 (1995).

[14] S.A.M. Mentink, G.J. Nieuwenhuys, A.A. Menovsky, J.A. Mydosh, A. Drost, E. Frikkee. Physica **B206/207**, 473 (1995).

[15] S.A.M. Mentink, H. Nakotte, A. de Visser, A.A. Menovsky, G.J. Nieuwenhuys, J.A. Nydosh. Physica **B186/188**, 270 (1993).

[16] C. Lacroix, B. Canals, M.D. Núñez-Regueiro. Phys. Rev. Lett. **77**, 5126 (1996).

[17] G.R. Stewart. Rev. Mod. Phys. **56**, 755 (1984).

[18] N. Grewe, F. Steglich. In: Handbook on the Physics and Chemistry of Rare Earths. V. 14 / Ed. by K.A. Gschneidner, Jr. and L. Eyring. Elsevier, Amsterdam (1991). P. 343.

[19] H.R. Ott, H. Rudiger, Z. Fisk, J.L. Smith. Phys. Rev. Lett. **50**, 1595 (1983).

[20] R. Troć, W. Trzebiatowski, K. Piprek. Bull. Acad. Polon. Sci., sér. sci. chim. **19**, 427 (1971).

[21] E. Bucher, J.P. Maita, G.W. Hull, R.C. Fulton, A.S. Cooper. Phys. Rev. **B11**, 440 (1975).

[22] U. Rauchschwalbe. Physica **B147**, 21 (1987).

[23] W. Suski. Lith. J. Phys. **37**, 21 (1997).

[24] S. Doniach. Physica **B91**, 231 (1977).

[25] A.V. Tiunis, V.A. Shaburov, Yu.P. Smirnov, A.E. Sovestnov, W. Suski, L. Folcik, Fiz. Tverd. Tela **38**, 1653 (1996).

[26] T. Nishioka, Y. Kurakahashi, R. Fukuda, M. Kotani. Czech. J. Phys. **46**, 2065 (1996).

[27] A. Krimmel, A. Severing, S. Spitzfaden, A. Grauel, B. Buschinger, C. Geibel, A. Loidl. Z. Phys. **B102**, 9 (1997).

[28] K. Umeo, H. Kadomatsu, T. Takabatake. J. Phys.: Cond. Matt. **8**, 9743 (1996).

[29] G.H. Lander, W.G. Stirling, S. Longridge, D. Gibbs. J. Magn. Magn. Mater. **140–144**, 1349 (1995).