Journal of Alloys and Compounds, 213/214 (1994) 243–247
JALCOM 4082

Magnetic anisotropy and transport properties of actinide intermetallics

L. Havela and V. Sechovský
Department of Metal Physics, Charles University, Ke Karlovu 5, 121 16 Prague 2 (Czech Republic)

H. Nakotte, E. Brück and F.R. de Boer
Van der Waals-Zeeman Laboratory, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam (Netherlands)

Abstract

Studies of actinide compounds point to a mutual relation between the coordination of An-ions in a crystal lattice and the orientation of the magnetic moment. Single-ion effects are thus not the dominant source of magnetic anisotropy. A hybridization induced anisotropy, which forces the magnetic moments to orient perpendicular to the An–An coordination direction, is compatible with experimental data. The An–An bonding anisotropy is thus reflected in magnetic-moment directions in magnetically ordered compounds, and the same type of anisotropy is revealed in the paramagnetic susceptibility. Consequently, Ising-like magnetism is manifest in compounds with a planar arrangement of U atoms (*e.g.* compounds with the ZrNiAl structure), whereas crystal structures, which can be viewed as consisting of linear U-chains, lead to a planar anisotropy. The latter class of compounds shows the influence of low-energy magnetic excitations in transport and thermodynamic properties. In contrast, no such effects are found in the uniaxial compounds because the magnitude of anisotropy energy E_a, which is of the order of hundreds of degrees kelvin, excludes magnon-like excitation with $E<E_a$.

1. Introduction

The large magnetic anisotropy in 5f band systems has been discussed theoretically in conjunction with a large orbital contribution to the magnetism in actinides by Brooks and Kelly [1]. They carried out electron structure calculations in the cubic systems UC and UN and obtained a large energy difference when the magnetic moments were confined in different crystallographic directions. From the practical point of view, the cubic symmetry of the crystal lattice is less suited for studies of magnetic anisotropy by bulk methods. Compounds with a symmetry lower than cubic frequently have the hard and easy magnetization directions perpendicular to each other, which makes the anisotropy more conspicuous.

We have been studying several types of compounds of the general formula UTX, which crystallize in hexagonal or orthorhombic structures, and can be characterized as narrow 5f-band systems. Investigations of the magnetic properties of these compounds have revealed two fundamental features of the magnetic anisotropy. First, it is very large (anisotropy energies of hundreds of degrees kelvin are observed as a rule). Second, the anisotropy is of the type which apparently reflects not the local symmetry at the actinide site, but something like the inter-actinide bonding symmetry. We show here some typical examples of magnetic anisotropy in actinide materials and discuss the relations to their crystal structures which suggest that the magnetic anisotropy is intimately connected with the bonding properties of 5f-electron states. Finally, we demonstrate how the type and strength of the magnetic anisotropy influence transport and thermodynamic properties at low temperatures.

2. Magnetic anisotropy of uranium equiatomic ternaries

Uranium equiatomic ternary compounds of the general formula UTX are formed in several different structure types. For X≡Al, Ga, Sn and In, and late transition metals T, the hexagonal ZrNiAl-type structure is formed as a rule. The degree of 5f delocalization can be tuned by a proper choice of T and X elements. For the T elements, the most important effect on the 5f states is the 5f–d hybridization, which depends strongly on the energy overlap of the 5f states and the d-states of the element T. The strength of the hybridization decreases for T elements with a higher atomic number in a given d series, because the d states

Elsevier Science S.A.
SSDI 0925-8388(94)04082-F

are pushed progressively towards higher binding energies. Thus, with some variability in both T and X components, the properties of the UTX compounds range from weak itinerant paramagnets (UFeAl) to magnetically ordered substances with well defined local moments (*e.g.* UNiGa) [2].

The ZrNiAl structure type can be viewed as consisting of two types of basal-plane sheets, separated by *c*/2. One sheet contains U-atoms and some of the T-atoms, and the other sheet contains only X- and T-atoms. Thus the inter-uranium spacing $d_{\text{U-U}}$ along the *c*-axis is equal to the lattice parameter *c* (typically 380–400 pm). Within the U–T sheet with $d_{\text{U-U}}$ typically 350–380 pm there are four nearest U neighbours. One can thus assume the 5f states to be involved in the bonding mainly within basal planes. This argument is supported by the possibility of hybridization of the 5f states with d states of transition metal atoms, occupying the positions within the U–T sheet. Direct evidence for the stronger U–T hybridization within the sheets is provided by polarized neutron diffraction experiments, which indicate significantly larger induced magnetic moments on the T-atoms within the U–T sheets, even in cases when the T-atoms occupying the T–X sheets are closer to U [3, 4]. In accordance with the common bonding anisotropy, we have found a strong uniaxial anisotropy in all U compounds of the ZrNiAl structure type [5]. Inspecting the dependence on field of the magnetization, we see that for a field along the *ab* plane the compounds behave as paramagnets even in a magnetically ordered state. In the case of ferromagnetic order we observe a spontaneous moment exclusively along the *c* axis and in antiferromagnets we can induce a spin-flip transition by applying a magnetic field along the *c* direction. The same type of anisotropy is also preserved in the paramagnetic region. The typical features are shown in Figs. 1 and 2 for the example of UNiAl, which is antiferromagnetic below 19 K. Studies of the onset of ferromagnetism, performed for example in the pseudoternary system $U(Ru_{1-x}Rh_x)Al$, show the appearance of ordered U moments of more than 1 μ_B oriented along the *c* axis in URhAl. However, the susceptibility for *B* perpendicular to *c* remains practically the same as in paramagnetic URuAl [6]. In most cases the $\chi(T)$ dependence for a field along the *c* direction (*i.e.* $\partial M^c/\partial H^c$ *vs.* *T*), obeys a Curie–Weiss law with θ_p of the order of tens of degrees kelvin either positive or negative, depending on the character of coupling. The susceptibility for a field perpendicular to the *c* axis is not only much smaller, but its character also resembles that of weakly temperature dependent paramagnets. However, an analysis in terms of the Curie–Weiss law is also feasible, and one can obtain values of effective moment μ_{eff} which are very similar for both field directions. The difference between both $\chi(T)$ branches is projected into the offset of θ_p, which is then very large. The difference $\Delta\theta_p = |\theta_p^c - \theta_p^{ab}|$ can be taken as a measure of the anisotropy in the paramagnetic state. However, for large anisotropy values, this quantity has a large uncertainty owing to the extrapolation procedure. Moreover, an error due to projection of the *c* axis susceptibility cannot be avoided owing to possible small grain misalignment and/or sample misorientation. Such spurious effects influence the hard axis data progressively as one approaches θ_p^c. Thus the value of $\Delta\theta_p$ yielded by the analysis can be understood approximately as a lower estimate of the anisotropy energy. The anisotropy field in the ordered state is usually estimated as the field which induces magnetic moments in the hard axis of the same size as found in the easy axis. Technically one has to extrapolate both branches of magnetization *vs.* field, $M^c(B)$ and $M^{ab}(B)$, so as to obtain an intercept. Because of eddy currents, the

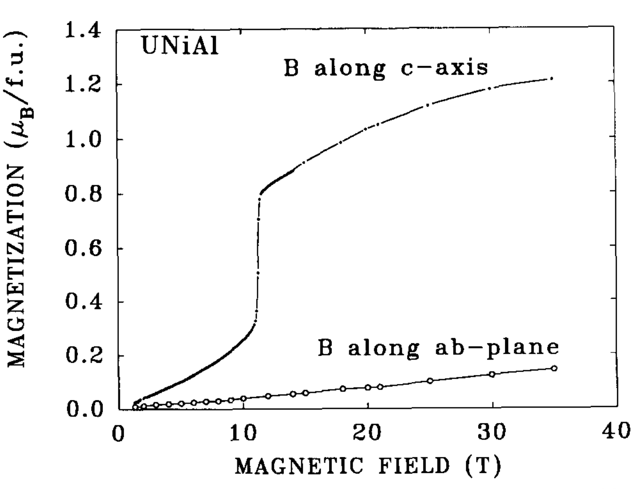

Fig. 1. Dependence on field of the magnetization of UNiAl at *T*=4.2 K for different field directions.

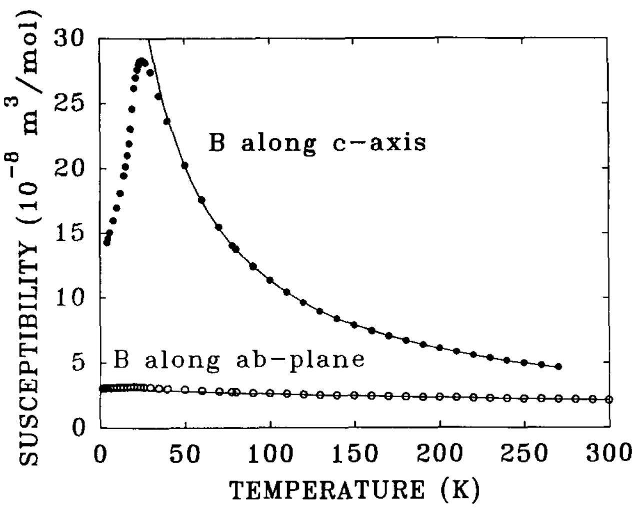

Fig. 2. Dependence on temperature of the magnetic susceptibility of UNiAl for different field directions.

magnetization of a single crystal can only be measured in field pulses of sufficient time duration. Practically, we are limited by the maximum field available in the Amsterdam High Field Installation (40 T). As we have to extrapolate to values of at least 300 T in some cases, the accuracy of our estimate is even worse than in the former case.

In addition to the anisotropy of the magnetic moment direction, we can also resolve the anisotropy of the mutual 5f–5f moments coupling. Magnetic structure investigations always show a dominating ferromagnetic coupling within the basal planes, whereas the coupling along the *c* axis can be either antiferromagnetic or ferromagnetic, and is generally much weaker.

A theory accounting for magnetic anisotropy in weakly delocalized materials has been developed by Cooper *et al.* [7]. Their approach is based on a hybridization-mediated anisotropic two-ion interaction, which originates from the anisotropic hybridization. Unlike the RKKY-type of interaction, this interaction is orbitally driven and leads to a strong ferromagnetic coupling along the bonding directions (directions of strong hybridization). The anisotropy can be viewed as due to charge compression towards the bonding directions, which fixes the orbital moments perpendicular to it. Assuming such an orientation of moments, a coupling favouring ferromagnetic pair moment alignment can be obtained. A hypothetical canting of moments from their minimum-energy directions leads to a moment decoupling or to a coupling to other, more remote, neighbours. For the group of UTX compounds crystallizing in the ZrNiAl structure type, this approach can explain both general findings, *i.e.* moments exclusively along *c* with a strong ferromagnetic coupling perpendicular to it.

To test this approach, we have made a comparative study of other groups of UTX compounds. Several compounds with late transition metals crystallize in the hexagonal structure of the $CaIn_2$ type (UPdSn, UAuSn, UCuSn, UPdSb) [8]. In contrast to the ZrNiAl type, here the U atoms form linear chains along the *c* direction with a large inter-chain separation, whereas the inter-U separation within the chains is rather moderate (about 360 pm). The magnetic structure of UAuSn is antiferromagnetic [9] with moments parallel along the orthorhombic *b* axis and a ferromagnetic coupling along the *c* axis, which conforms to the rules of the model given above. In UPdSn, moments do not lie completely in the *bc* plane [10]. The magnetic structure is non-collinear with alternating rings of the inclination angles to the *ab* plane. However, the *c* axis is unambiguously a hard-magnetization direction. The anisotropy energy estimate is lower than for the former group of compounds (60 K or 110 T). In comparison with UAuSn, it is not clear whether the non-collinear structure of UPdSn is due only to a higher degree of 5f localization [11], or whether the presumably less localized UAuSn would adopt a similar magnetic structure if it were allowed by the crystal symmetry (UPdSn has a lower symmetry of crystal structure as it is, unlike UAuSn, an ordered ternary compound).

The last case we discuss here are compounds with the orthorhombic structure of the TiNiSi type, which are formed by similar T elements, but for X≡Si or Ge. The bonding symmetry is analogous to the previous case, although the chains stretched along the *a* axis are not really in one line but are zig-zag, and the inter-chain spacing is somewhat smaller. Neutron diffraction studies show that moments in the compounds studied are confined within the *bc* plane [12–15]. Single-crystal magnetization data, available for UNiGe (see Figs. 3 and 4) show that there is a moderate anisotropy in the *bc* plane ($\Delta\theta_p^{bc} = |\theta_p^c - \theta_p^b| \approx 40$ K), but inspection of the *a*-axis data reveals an anisotropy of about 140 K (equal to $\Delta\theta_p^{ac}$).

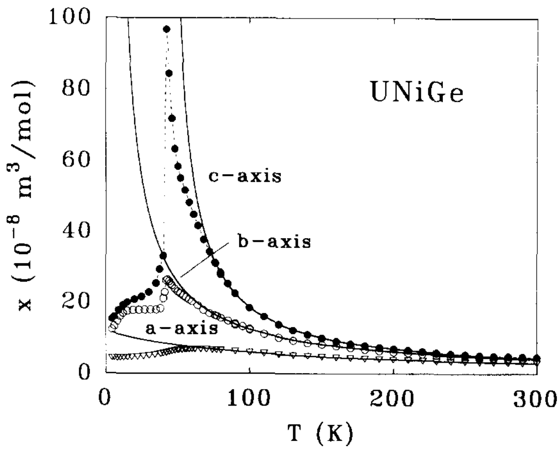

Fig. 3. Dependence on temperature of the magnetic susceptibility of UNiGe for different field directions.

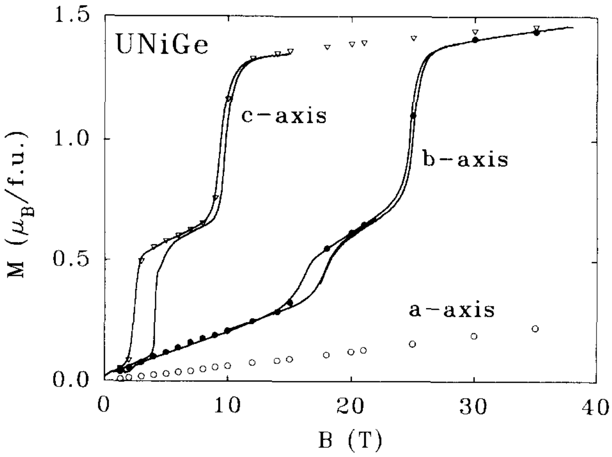

Fig. 4. Dependence on field of the magnetization of UNiGe at $T = 4.2$ K for different field directions.

From the information above we can thus deduce that the anisotropy in U compounds is indeed related to the "bonding anisotropy". Thus it is predominantly the coupling between nearest U neighbours forcing the U-moments to orient perpendicular to the strong U–U bonds. This conclusion applies generally, wherever a simple linear or planar arrangement of nearest U atoms occurs (*e.g.* UGa_2 or even heavy fermion compounds UPt_3 and UPd_2Al_3). For the linear arrangement some in-plane anisotropy can also be found, but its magnitude is much smaller than the basic anisotropy confining the moments in the plane.

It is interesting to compare the effects of low-energy magnetic excitations on the bulk properties of the two classes of compounds. In the planar-anisotropy case, one should be able to observe magnons or similar excitations with a gap in the energy spectrum. The gap width Δ can be associated with the energy of the in-plane anisotropy. For moderate Δ values one should observe an additional exponential term in the temperature dependence of electrical resistivity (owing to the electron–magnon scattering), and the magnon excitations should contribute to the specific heat. Assuming a simple quadratic magnon dispersion $\hbar\omega_q = \Delta + \hbar^2 q^2/2m_0$ and a q-independent electron–magnon coupling constant, one can find the expressions $\rho_{e\text{-}magn} = bT(1+2T/\Delta)\exp(-\Delta/T)$ and $C_{magn} = fT^{1/2}\exp(-\Delta/T)$ [16], which account well for the experimental data of UNiGe, UPdSn, etc. The values of Δ obtained from analysis of the electrical resistivity and specific heat data are similar and, moreover, correspond well with the estimate of the in-plane anisotropy energy (35–50 K for the compounds mentioned above) [17].

From what has been stated here for compounds with the ZrNiAl structure type, they can be characterized as Ising systems, where very strong uniaxial anisotropy prohibits excitation of magnons. Indeed, analysis of the low temperature data of UNiGa shows that possible exponential terms are difficult to detect within the experimental uncertainty, which means that no magnon modes with Δ smaller than approximately 200 K can exist. An open question remains: how far are the mentioned bulk properties affected by the detailed nature of magnetic excitations in actinides? This is a more complex subject [18].

3. Conclusions and future perspectives

Although the presented model, relating the magnetic anisotropy to a bonding anisotropy, works well for a large number of U-compounds and enables easy predictions of the anisotropy type, it is not clear *a priori* which are the most decisive factors determining a real bonding anisotropy. In particular, it is not possible to guess how far the bonding strength is assisted by the hybridization with the d states or, in another words, what is the importance of a symmetric layout of the non-f ligands. To shed more light on this issue we have been searching for compounds displaying different basic arrangements, *i.e.* planar or linear, within a single structure type. The recently discovered system of U_2T_2X compounds [19, 20] offers such a possibility. These compounds crystallize in the U_3Si_2 structure type (tetragonal), where a proper choice of ligands leads to compounds with nearest U neighbours either within the basal plane or along the *c* direction. The cross-over can be found, for example between U_2Pd_2Sn and U_2Pt_2Sn, and we will concentrate more on these systems in future.

Acknowledgments

This work has been supported by the "Stichting voor Fundamenteel Onderzoek der Materie" (FOM) and by the Grant Agency of the Czech Republic (project No. 202/93/0184). L.H. and V.S. were also supported by the Alexander von Humboldt Foundation.

References

1 M.S.S. Brooks and P.J. Kelly, *Phys. Rev. Lett., 51* (1983) 170B.

2 V. Sechovsky and L. Havela, Intermetallic compounds of actinides. In E.P. Wohlfarth and K.H.J. Buschow (eds.), *Ferromagnetic Materials*, Vol. 4, North-Holland, Amsterdam, 1988, pp. 309–491.

3 J.A. Paixão, G.H. Lander, P.J. Brown, H. Nakotte, F.R. de Boer and E. Brück, *J. Phys. Condens. Matter, 4* (1992) 829.

4 J.A. Paixão, G.H. Lander, P.J. Brown, H. Nakotte, F.R. de Boer and E. Brück, *Europhys. Lett. 24* (1993) 607.

5 L. Havela, V. Sechovsky, F.R. de Boer, E. Brück and H. Nakotte, *Physica B, 177* (1992) 159.

6 P.A. Veenhuizen, F.R. de Boer, A.A. Menovsky, V. Sechovsky and L. Havela, *J. Phys. (Paris) Coll., C8* (1988) 1485.

7 B.R. Cooper, R. Siemann, D. Yang, P. Thayamballi and A. Banerjea, Hybridization-induced anisotropy of cerium and actinide systems. In A.J. Freeman and G.H. Lander (eds.), *Handbook on the Physics and Chemistry of the Actinides*, Vol. 2, North-Holland, Amsterdam, 1985, pp. 435–500.

8 F.R. de Boer, E. Brück, H. Nakotte, A.V. Andreev, V. Sechovsky, L. Havela, P. Nozar, C.J.M. Denissen, K.H.J. Buschow, B. Vaziri, M. Meissner, H. Maletta and P. Rogl, *Physica B, 176* (1992) 275.

9 R.A. Robinson, J.W. Lynn, V. Nunez, K.H.J. Buschow, H. Nakotte and A.C. Lawson, *Phys. Rev. B, 47* (1993) 5090.

10 R.A. Robinson, A.C. Lawson, K.H.J. Buschow, F.R. de Boer, V. Sechovsky and R.B. Von Dreele, *J. Magn. Magn. Mater., 98* (1991) 147.

11 L. Havela, V. Sechovsky, J.R. Naegele, T. Almeida, E.H. Brück, H. Nakotte and F.R. de Boer, *J. Magn. Magn. Mater., 104–107* (1992) 23.

12 R.A. Robinson, A.C. Lawson, J.W. Lynn and K.H.J. Buschow, *Phys. Rev. B, 47* (1993) 6138.

13 S. Kawamata, K. Ishimoto, Y. Yamaguchi and T. Komatsubara, *J. Magn. Magn. Mater., 104–107* (1992) 51.

14 A. Murasik, P. Fischer, R. Troc and V.H. Tran, *J. Phys. Condens. Matter, 3* (1991) 1841.

15 V. Sechovsky, L. Havela, K. Prokes, H. Nakotte, E. Brück, F.R. de Boer, P. Svoboda and H. Maletta, *Proc. 23ème Journée des Actinides, Schwarzwald, 1993.*

16 N. Hessel Andersen and H. Smith, *Phys. Rev. B, 19* (1979) 384.

17 L. Havela, V. Sechovsky, H. Nakotte, E. Brück and K. Prokes, *Proc. 23ème Journée des Actinides, Schwarzwald, 1993.*

18 G.H. Lander and G. Aeppli, *J. Magn. Magn. Mater., 100* (1991) 151.

19 F. Mirambet, P. Gravereau, B. Chevalier, L. Trut and J. Etourneau, *J. Alloys Comp., 191* (1993) L1.

20 M.N. Peron, Y. Kergadallan, J. Rebizant, D. Meyer, S. Zwirner, L. Havela, H. Nakotte, J.C. Spirlet, G.M. Kalvius, E. Collineau, J.L. Oddou, C. Jeandey, J.P. Sanchez and J.M. Winand, *J. Alloys Comp.,* in press.