Thermal expansion of single-crystalline UNiAl

Prokes, K.; de Visser, A.; Menovsky, A.A.; Brück, E.H.; de Boer, F.R.; Sechovsky, V.; Gortenmulder, T.

DOI
10.1063/1.361999

Publication date
1996

Published in
Journal of Applied Physics

Thermal expansion of single-crystalline UNiAl

K. Prokeš, A. de Visser, A. A. Menovsky, E. Brück, and F. R. de Boer
Van der Waals-Zeeman Institute, University of Amsterdam, 1018 XE Amsterdam, The Netherlands

V. Sechovský
Department of Metal Physics, Charles University, 12116 Prague 2, The Czech Republic

T. J. Gortenmulder
Kamerlingh Onnes Laboratory, University of Leiden, 2300 RA Leiden, The Netherlands

Magnetization, magnetic susceptibility, electrical resistivity, and specific heat measurements of UNiAl point to antiferromagnetic ordering below 19.3 K, which is confirmed by neutron-diffraction experiments. The enhanced γ value of 167 mJ/mol K^2 is reflecting pronounced presence of magnetic fluctuations, which influence also the other electronic properties down to low temperatures. The thermal expansion of UNiAl was measured in the temperature range 1.5–210 K on a single crystal along the *a* and *c* axis. Similar to other bulk properties, also the thermal expansion of UNiAl is highly anisotropic. The *a* axis is monotonously expanding with increasing temperature in the whole temperature range. Along the *c* axis, the lattice first collapses with increasing temperature up to 35 K. Around this temperature, the thermal expansion coefficient α_c changes sign and continuous expansion with further increasing temperature is then observed. The sharp anomaly of α near 19.3 K present in both directions is consistent with the magnetic phase transition. The results are discussed in terms of the presence of anisotropic magnetic fluctuations. [S0021-8979(96)25708-5]

I. INTRODUCTION

The study of the formation of U magnetic moments in intermetallic compounds plays an essential role in understanding the electronic properties of *f*-electron-based systems, specially because of possible participation of U $5f$-electrons in the bonding. It has been well established that the variation of the constituent elements in UTX (T=a transition metal, X=a metal from the *p*-block) intermetallic compounds can drastically change the type of ground state due to the influence of the *d*- and *p*-electron states of these elements on the $5f$ electron states, which are principally involved in magnetism.[1] Also when keeping one type of crystal structure (fixed geometry of the surrounding of the U atom) a broad scale of magnetic behavior ranging from Pauli paramagnetism through spin fluctuations towards local-$5f$-moment behavior and magnetic ordering can be observed.

Another essential issue in U intermetallics is the huge magnetocrystalline anisotropy, which originates from the anisotropic bonding of the $5f$ wave functions in the crystal and from considerable $5f$-orbital moments. Among the highly anisotropic UTX compounds crystallizing in the hexagonal ZrNiAl-type of structure (Fig. 1), UNiAl has attracted considerable attention because of the highest γ value of 167 mJ/mol K^2 in this isostructural group of compounds. In the literature,[1,2] this enhanced γ value qualifies UNiAl as a middle-weight heavy-fermion system.

UNiAl becomes antiferromagnetic below 19.3 K as has been inferred from the magnetization, magnetic susceptibility, specific heat and electrical resistivity behavior.[2] It exhibits a strong uniaxial magnetic anisotropy with the easy-magnetization direction along the *c* axis, which is reflected also in transport properties. The magnetic structure of UNiAl consists of the U magnetic moments oriented along the *c* axis modulated sinusoidally within the basal planes and coupled antiferromagnetically between these planes. The propagation vector is $\mathbf{k}=(0.1,0.1,0.5)$. The numerous indications of strong involvement of magnetic fluctuations in low-temperature electronic properties[2] make this compound attractive for further experimental investigations and theoretical treatment.

Here, we report the first thermal expansion measurements performed on a single crystal of UNiAl.

II. EXPERIMENT

A single crystal of UNiAl was grown from a nonstoichiometric melt with a slight excess of U by a modified Czochralski technique in the Center ALMOS at the University of Amsterdam. In order to reduce the mosaicity, the seed was tilted from the easy-growth direction by an angle of about 15°. The quality of the resulting crystal was checked by x-ray diffraction and electron-microprobe analysis. It was

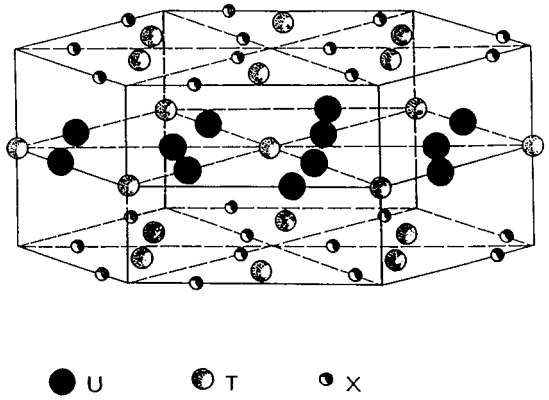

FIG. 1. Schematic representation of the ZrNiAl-type of structure.

 0021-8979/96/79(8)/6358/3/$10.00

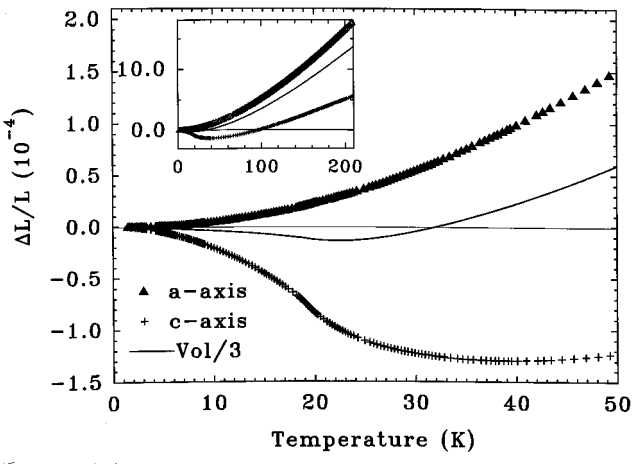

FIG. 2. Temperature dependence of the change of the relative length with respect to 1.5 K measured on a UNiAl single crystal along the a axis (Δ) and the c axis ($+$), and temperature dependence of the relative volume change (—).

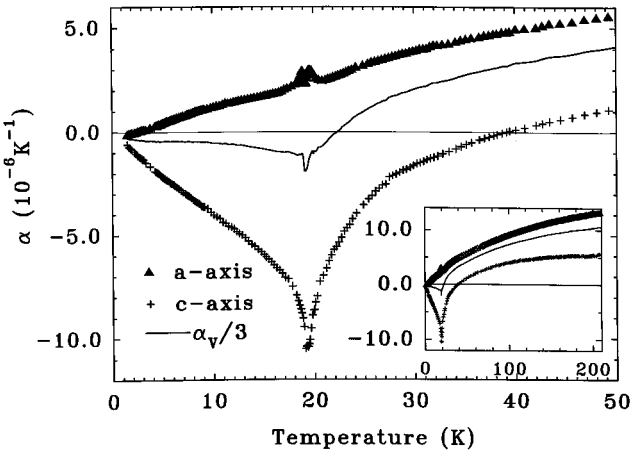

FIG. 3. Temperature dependence of the thermal expansion coefficients along the a axis α_a (Δ) and along the c axis α_c ($+$) measured on a UNiAl single crystal. The corresponding coefficient of the volume expansion $\alpha_V(T)=2\alpha_a(T)+\alpha_c(T)$ is given by the solid line.

found to be single-crystalline; however, a certain amount of included pure U was detected by the electron-microprobe analysis.

By means of spark erosion a semi-cube with a size of each side of about 3.8 mm was cut perpendicular to the a and the c axes. The temperature dependence of the thermal expansion along the a axis $\alpha_a(T)$ and along the c axis $\alpha_c(T)$ was measured with a parallel-plate capacitance method[3] in the temperature range 1.5–210 K. The temperature was changed in steps and stabilised in order to keep the thermal equilibrium of sample and cell during the measurement. The relative accuracy decreases with increasing temperature, reaching a limit in α of about $3\ 10^{-7}\ \mathrm{K}^{-1}$ around 100 K.

III. RESULTS AND DISCUSSION

The temperature dependence of the relative length changes, $(\Delta L/L)_i$ with respect to the length of the sample along the particular direction at 1.5 K are displayed in Fig. 2 together with the relative volume change $(\Delta V/V)=2(\Delta L/L)_a+(\Delta L/L)_c$. The temperature dependence of the coefficient of linear thermal expansion, $\alpha_i=L_i^{-1}(dL_i/dT)$, where i refers to the a or the c axis of the hexagonal UNiAl, is shown in Fig. 3. The corresponding coefficient of volume expansion $\alpha_V(T)=2\alpha_a(T)+\alpha_c(T)$ is given by the solid line.

As can be seen, the thermal expansion of UNiAl is highly anisotropic, similar to most of other bulk properties. Along the a axis the lattice monotonously expands with increasing temperature (α_a is always positive). The c axis direction reveals first considerable shrinking with increasing temperature yielding a sharp deep minimum at 19.3 K. Around 35 K, $\alpha_c(T)$ changes sign and the lattice expands at higher temperatures. The sharp anomaly observed at 19.3 K in both $\alpha_a(T)$ and $\alpha_c(T)$ is consistent with the magnetic phase transition. In the case of the a-axis direction, the anomaly is doubled. As the absolute value of $\alpha_c(T)$ is considerably larger than $\alpha_a(T)$, the coefficient of volume expansion $\alpha_V(T)$ is negative below 22 K. The maximum anisotropy, corresponding to the maximum difference $\alpha_a(T)-\alpha_c(T)$, is found at T_N. At high temperatures, both thermal expansion coefficients can be approximated by a Debye function with distinct Debye temperatures. The best agreement at temperatures above 80–90 K for the coefficient along the c axis is achieved for $\Theta_D=280$ K. For the coefficient along the a axis, a much higher value of $\Theta_D=400$ K is obtained. In this case, the satisfactory agreement is restricted to region above 150 K.

At low temperatures, both $\alpha_a(T)$ and $\alpha_c(T)$ can be approximated by a linear dependence. By fitting in the temperature region 1.5–4 K, the linear coefficients of the thermal expansion $a_a=\alpha_a(T)/T=1.69\times10^{-7}\ \mathrm{K}^{-2}$ and $a_c=\alpha_c(T)/T=-4.57\times10^{-7}\ \mathrm{K}^{-2}$ are obtained, yielding $a_V=2a_a+a_c=-1.19\times10^{-7}\ \mathrm{K}^{-2}$.

The effective Grüneisen parameter $\Gamma_{\mathrm{eff}}(T)$[4]

$$\Gamma_{\mathrm{eff}}(T)=V_m\alpha_V(T)/\kappa c(T), \tag{1}$$

where V_m is the molar volume, $\kappa=-V^{-1}(dV/dp)$ is the isothermal compressibility, and $c(T)$ is the molar specific heat at constant volume, is a parameter which is frequently discussed in the context of heavy-fermion research. The experimental effective Grüneisen parameter $\Gamma_{\mathrm{eff}}(T)$ is in general temperature dependent and consists of several contributions. In the low-temperature limit where the specific heat and thermal expansion vary linearly, the effective Grüneisen parameter $\Gamma_{\mathrm{eff}}(T)$ is driven by the electronic term $\Gamma_e(T)$

$$\Gamma_e=V_m a_V/\kappa\gamma. \tag{2}$$

In the case of UNiAl, the value of the isothermal compressibility is not available and has to be estimated. We have used a value close to that observed for URhAl[5] which amounts to 1.0 Mbar^{-1}. The specific-heat data from Brück *et al.*[2] provide $\gamma=167$ mJ/mol K^2, $V_m=3.18\times10^{-5}$ m^3/mol. Using Eq. (2) we derive for UNiAl $\Gamma_e=-6.8$. This value is about one order of magnitude smaller than for typical heavy-fermion compounds, e.g., UPt_3,[4] although it is considerably enhanced with respect to normal metals ($\Gamma_e\sim2$). It also should be noted that the relatively small value of α_V is a consequence

of mutual cancellation of significantly large coefficients α_a and α_c, one positive and the other negative. Especially, α_c is very large in absolute value indicating a very strong magnetoelastic coupling along c.

It has been pointed out by Brück *et al.*[2] that UNiAl can be classified as an itinerant antiferromagnet with strong indications for the presence of spin fluctuations. Therefore, a partial contribution to α and Γ due to the spin fluctuations is most probable to play an important role in UNiAl. For the characteristic temperature of the spin fluctuations in UNiAl, a value of the order of 10 K follows from the specific-heat data. The electrical resistivity and the magnetic susceptibility data strongly support this conclusion. One can perform an analysis of all the bulk data together with thermal-expansion results using the so-called universal relations which couple the magnetic susceptibility, the specific heat or the electrical resistivity with thermal-expansion data.[6] However, to draw clear conclusions, usually inelastic-neutron-scattering experiments are necessary.

Recently, we have performed both, elastic and inelastic-neutron-scattering experiments on a good-quality UNiAl single crystal.[7] Here we summarize only the points relevant to understand the thermal-expansion results. The analysis of the neutron-diffraction results reveals the presence of strong antiferromagnetic fluctuations in UNiAl. The development of the fluctuations with temperature can be followed from low temperatures up to at least $1.5T_N$. However, no particular dispersion can be assigned to magnetic fluctuations. Instead of that, a wide spread in energy transfer of scattering intensity is present in the inelastic spectrum, both, below and above T_N.

As the magnetocrystalline anisotropy of UNiAl expressed in values of the paramagnetic Curie temperature reaches 300–400 K, the magnetic fluctuations have entirely different behavior along the c axis and within the basal plane. The onset of magnetic fluctuations is visible around 35–40 K where upon lowering the temperature a deviation from the high-temperature behavior of the thermal-expansion coefficient α_a can be observed accompanied by a contraction along the hexagonal axis. Magnetic fluctuations along the c axis are clearly of antiferromagnetic type. The behavior along the a axis is rather regular, except for the critical region around T_N.

IV. CONCLUSION

We have shown that the thermal expansion of UNiAl which crystallizes in the hexagonal ZrNiAl-type of structure is large and highly anisotropic. The magnetic phase transition at 19.3 K is reflected in both directions by a pronounced anomaly. These findings are in good agreement with other bulk magnetic, transport and thermal properties which reflect the huge magnetocrystalline anisotropy as well. The magnetic structure consists of sine-modulated U magnetic moments within the basal plane with adjacent planes coupled antiferromagnetically.

The value of the electronic contribution to the Grüneisen parameter $\Gamma_e = -6.8$ is relatively small compared to values observed for typical heavy-fermion compounds. This is, however, partially due mutual cancellation of the expansion effects along a and c. The large negative expansion along c below 35 K, on the other hand, can be tentatively attributed to the effect of antiferromagnetic fluctuations and to antiferromagnetic ordering in UNiAl below 19.3 K.

ACKNOWLEDGMENTS

This work was sponsored by the ''Stichting voor Fundamenteel Onderzoek der Materie'' (FOM), and The Grant Agency of the Czech Republic (project # 202/94/0454). The authors are indebted to Dr. M. Diviš for stimulating discussions on the subject.

[1] V. Sechovský and L. Havela, *Ferromagnetic Materials*, edited by E. P. Wolfarth and K. H. J. Buschow (North-Holland, Amsterdam, 1988), Vol. 4, Chap. 4.
[2] E. Brück, H. Nakotte, F. R. de Boer, P. F. de Châtel, H. P. van der Meulen, J. J. M. Franse, A. A. Menovsky, N. H. Kim-Ngan, L. Havela, V. Sechovský, J. A. A. J. Perenboom, N. C. Tuan, and J. Šebek, Phys. Rev. B **49**, 8852 (1994).
[3] See for instance, N. H. van Dijk, Ph.D. thesis, University of Amsterdam, 1994.
[4] A. de Visser, J. J. M. Franse, and J. Flouquet, Physica B **161**, 324 (1989).
[5] T. D. Cuong, Z. Arnold, J. Kamarád, A. V. Andreev, L. Havela, and V. Sechovský, EMMA'95, J. Magn. Magn. Mater. (in press).
[6] A. de Visser, A. Menovsky, and J. J. M. Franse, Physica B **147**, 81 (1987).
[7] K. Prokeš *et al.* (to be published).