Dilatometry study of the ferromagnetic order in single-crystalline URhGe

S. Sakarya* and N. H. van Dijk

Interfaculty Reactor Institute, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands

A. de Visser and E. Brück

Van der Waals–Zeeman Institute, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

Thermal expansion measurements have been carried out on single-crystalline URhGe in the temperature range from 2 to 200 K. At the ferromagnetic transition (Curie temperature $T_C = 9.7$ K), the coefficients of linear thermal expansion along the three principal orthorhombic axes all exhibit pronounced positive peaks. This implies that the uniaxial pressure dependencies of the Curie temperature, determined by the Ehrenfest relation, are all positive. Consequently, the calculated hydrostatic pressure dependence dT_C/dp is positive and amounts to 0.12 K/kbar. In addition, the effective Grüneisen parameter was determined. The low-temperature electronic Grüneisen parameter $\Gamma_{sf} = 14$ indicates an enhanced volume dependence of the ferromagnetic spin fluctuations at low temperatures. Moreover, the volume dependencies of the energy scales for ferromagnetic order and ferromagnetic spin fluctuations were found to be identical.

I. INTRODUCTION

Recently, the intermetallic compound URhGe has attracted much attention because superconductivity ($T_c = 0.25$ K) was found to coexist with ferromagnetism (Curie temperature $T_C = 9.5$ K).[1] The surprising discovery of superconductivity at ambient pressure in this itinerant ferromagnet was preceded by the discovery of (pressure-induced) superconductivity in the itinerant ferromagnets UGe$_2$ (Ref. 2) and ZrZn$_2$ (Ref. 3). Until these discoveries, it was generally believed that ferromagnetic order excludes superconductivity. This is nicely demonstrated by the experiments on ErRh$_4$B$_4$ (Refs. 4 and 5) and HoMo$_6$S$_8$ (Ref. 6), where standard BCS singlet-type superconductivity is suppressed when ferromagnetic order sets in. The most likely explanation for the appearance of superconductivity in these weak itinerant ferromagnets is that the superconducting state is mediated by ferromagnetic spin fluctuations, giving rise to Cooper pairs with parallel spins ($S = 1$).[7–10] This type of pairing is relatively insensitive to a local magnetic field and can therefore coexist with ferromagnetic order. The pressure-dependent experiments on UGe$_2$ and ZrZn$_2$ suggest that in these systems superconductivity emerges near a ferromagnetic quantum critical point, i.e., when the ferromagnetic transition temperature is tuned to $T_C = 0$. At the quantum critical point the ferromagnetic spin fluctuations are strongly enhanced. One may therefore expect that ferromagnetic order in URhGe is also very sensitive to pressure.

URhGe crystallizes in the orthorhombic TiNiSi-type structure (space group P_{nma}).[11] The unit cell, with dimensions $a = 6.87$ Å, $b = 4.33$ Å, and $c = 7.51$ Å, contains four formula units. Neutron-diffraction experiments on single-crystalline URhGe (Ref. 12) revealed a collinear ferromagnetic order below $T_C = 9.6$ K with ordered U moments of $0.35\mu_B$ confined to the b-c plane. No component of the ordered moment was observed along the a axis, which acts as the hard magnetic direction for the magnetization. In addition to the neutron-diffraction experiments, the ferromag-

netic order in single-crystalline URhGe was studied by specific heat, magnetization, and electrical resistivity,[12,13] which showed a sizeable influence of applied magnetic fields on the ferromagnetic order and on the ferromagnetic spin fluctuations in the b-c plane. In the low-temperature limit, the specific heat is characterized by the electronic contribution of the ferromagnetic spin fluctuations with a moderately enhanced linear term of $\gamma = 164$ mJ/mol K^2. The magnetic properties of single-crystalline URhGe are in good agreement with the results from earlier measurements on polycrystalline and powder samples,[14–19] which have been reviewed by Sechovsky and Havela.[11] Recently, band-structure calculations were performed by Divis and co-workers[20] and Shick[21] to study the origin of the magnetic order in URhGe. These calculations suggest a substantial hybridization between the U-5f and Rh-4d states and a relatively small Uranium magnetic moment of 0.3 μ_B due to a partial cancellation of the spin and orbital components. The calculated moments are in good agreement with the measured values.

In this paper we report thermal expansion measurements of single-crystalline URhGe in the temperature range from $T = 2$ to 200 K. Our principal aim was to determine the pressure dependence of the ferromagnetic transition temperature T_C. For a second-order phase transition, the uniaxial pressure dependence of T_C (at ambient pressure) can be determined with the Ehrenfest relation from the anomalies in the linear coefficient of thermal expansion and the specific heat. The initial pressure dependence may give an estimate of the critical pressure needed to suppress the ferromagnetic order and reach the quantum critical point at $T_C = 0$. In addition, we have determined the electronic Grüneisen parameter, which characterizes the volume dependence of the ferromagnetic spin fluctuations at low temperatures.

II. EXPERIMENT

The dilatometry experiments were performed on a single-crystalline URhGe sample with dimensions $a \times b \times c = 2.4$
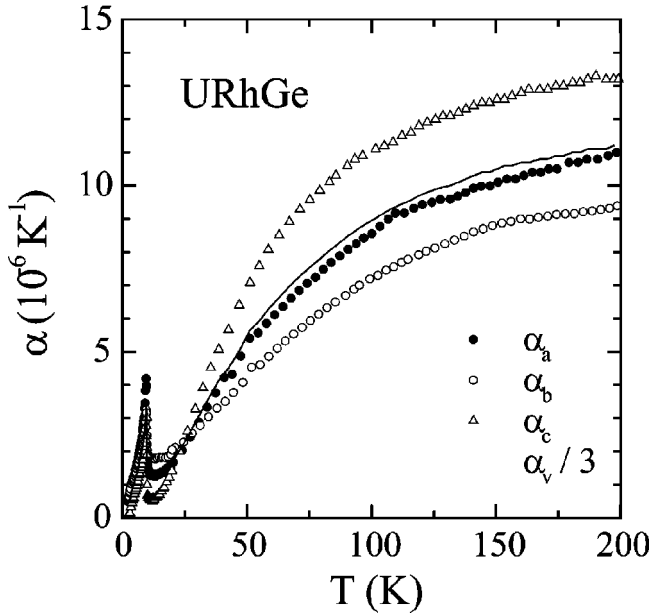
FIG. 1. The coefficients of linear thermal expansion α of URhGe as a function of temperature T along the orthorhombic a, b, and c axis. For comparison the volume expansion divided by a factor 3 ($\alpha_v/3$) is also shown. The high-temperature behavior is governed by the phonon contribution, while the anomaly at $T_C = 9.7$ K reflects the onset of ferromagnetic order.

$\times 5.0 \times 2.4$ mm^3. The sample was cut from the material used in earlier specific-heat measurements performed by Hagmusa and co-workers.[13] The crystal has been grown from a stoichiometric melt of at least 99.95% pure materials by means of a modified tetra-arc Czochralski technique in a continuous gettered Ar atmosphere. No subsequent heat treatment was given to the crystal. Due to the relatively high residual resistivity at low temperatures no superconductivity was observed in this particular crystal.[12] The coefficient of linear thermal expansion $\alpha(T) = (1/L)(dL/dT)$ was measured, using a sensitive parallel-plate capacitance dilatometer[22] along the orthorhombic a, b, and c axis of the crystal. From these measurements the volume expansion $\alpha_v = \alpha_a + \alpha_b + \alpha_c$ was determined.

III. RESULTS

In Fig. 1 the coefficient of linear thermal expansion α along the a, b, and c axis of single-crystalline URhGe is shown as a function of temperature in the range from $T = 2$ to 200 K. The temperature dependence of the volume expansion $\alpha_v = \alpha_a + \alpha_b + \alpha_c$ is shown for comparison (notice the figure shows $\alpha_v/3$). At high temperatures the thermal expansion is governed by the phonon contribution for all three orientations. Around a temperature of 25 K a remarkable crossing of the curves for the thermal expansion along the a, b, and c axis is observed. This crossing is a clear sign for the development of an additional contribution from ferromagnetic spin fluctuations at low temperatures. It is interesting to note that this additional contribution from ferromagnetic spin fluctuations mainly affects the anisotropy of the thermal ex-
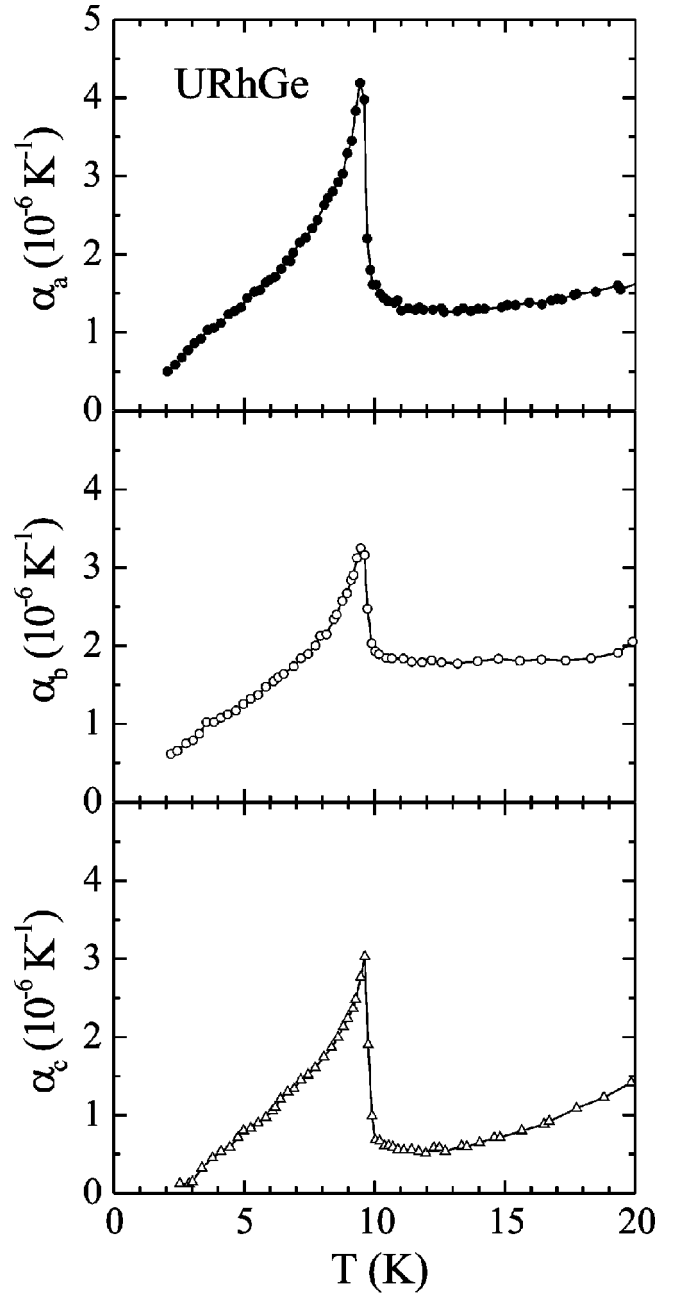

FIG. 2. The coefficients of linear thermal expansion α of URhGe as a function of temperature T along the orthorhombic a, b, and c axis at low temperatures. The anomaly at $T_C = 9.7$ K reflects the onset of ferromagnetic order. The large linear term at low temperatures is due to spin fluctuations.

pansion in the b-c plane, which acts as the easy plane for the magnetization. At $T_C = 9.7$ K the ferromagnetic order sets in and a peak in the coefficient of linear thermal expansion is observed for all three directions.

The low-temperature behavior of the coefficients of linear thermal expansion along the a, b, and c axis is shown in more detail in Fig. 2. The observed steps in the coefficients of linear thermal expansion have the same sign but different sizes for the three orthorhombic axes of single-crystalline URhGe. The values of the steps are listed in Table I. In Fig.

TABLE I. Step anomalies in the coefficients of linear thermal expansion of single-crystalline URhGe along the orthorhombic a, b, and c axis. The corresponding pressure dependence of the Curie temperature, dT_C/dp, was deduced from the Ehrenfest relation (see text).

	$\Delta \alpha$ (10^{-6}K^{-1})	dT_C/dp (K/kbar)
a axis	3.4(1)	0.052(3)
b axis	1.7(1)	0.026(2)
c axis	2.7(1)	0.041(2)
Volume	7.8(2)	0.119(6)

3 the low-temperature volume expansion divided by temperature (α_v/T) is shown as a function of temperature and compared with the specific heat divided by temperature (c/T) measured on a sample prepared from the same single-crystalline batch.[13]

IV. DISCUSSION

The temperature dependence of the thermal expansion at high temperatures is governed by the phonon contribution and closely resembles a Debye curve. The estimated Debye temperature of $\theta_D \approx 200$ K is in good agreement with the specific heat data.[12,13] At low temperatures the Debye curve for the phonon contribution is expected to show a T^3 temperature dependence. Below $T = 30$ K the thermal expansion along the a axis shows a clear deviation of this behavior, which is even more pronounced along the b axis. This deviation indicates the development of an additional contribution due to ferromagnetic spin fluctuations. This additional contribution was also observed in the specific heat measurements and described in terms of an enhanced electronic contribution.[12] In the ferromagnetically ordered state below $T_C = 9.7$ K, the temperature dependence of the volume expansion closely resembles that of the specific heat, as shown in Fig. 3. In line with the analysis of the specific heat measurements,[12] three different contributions to the thermal expansion can be identified in the ferromagnetically ordered state, namely, contributions due to phonons, ferromagnetic spin waves, and ferromagnetic spin fluctuations. As discussed, the phonon contribution shows a T^3 power-law behavior at low temperatures. The ferromagnetic spin-wave contribution is expected to obey a $T^{3/2}$ power-law behavior, while the ferromagnetic spin fluctuations lead to an enhanced linear term at low temperatures. Both the phonon and spin-wave contributions to the volume expansion divided by temperature (α_v/T) [and the specific heat divided by temperature (c/T)] vanish at low temperatures and, as a consequence, the extrapolated value of $\alpha_v/T = 5.8(2) \times 10^{-7}$ K^{-2} at $T = 0$ is solely due to the contribution of the ferromagnetic spin fluctuations. As expected for an itinerant ferromagnetic system, no indications of a crystal field contribution were observed in the temperature dependence of the coefficients of linear thermal expansion.

In order to determine the uniaxial and hydrostatic pressure dependence of the ferromagnetic transition temperature, we
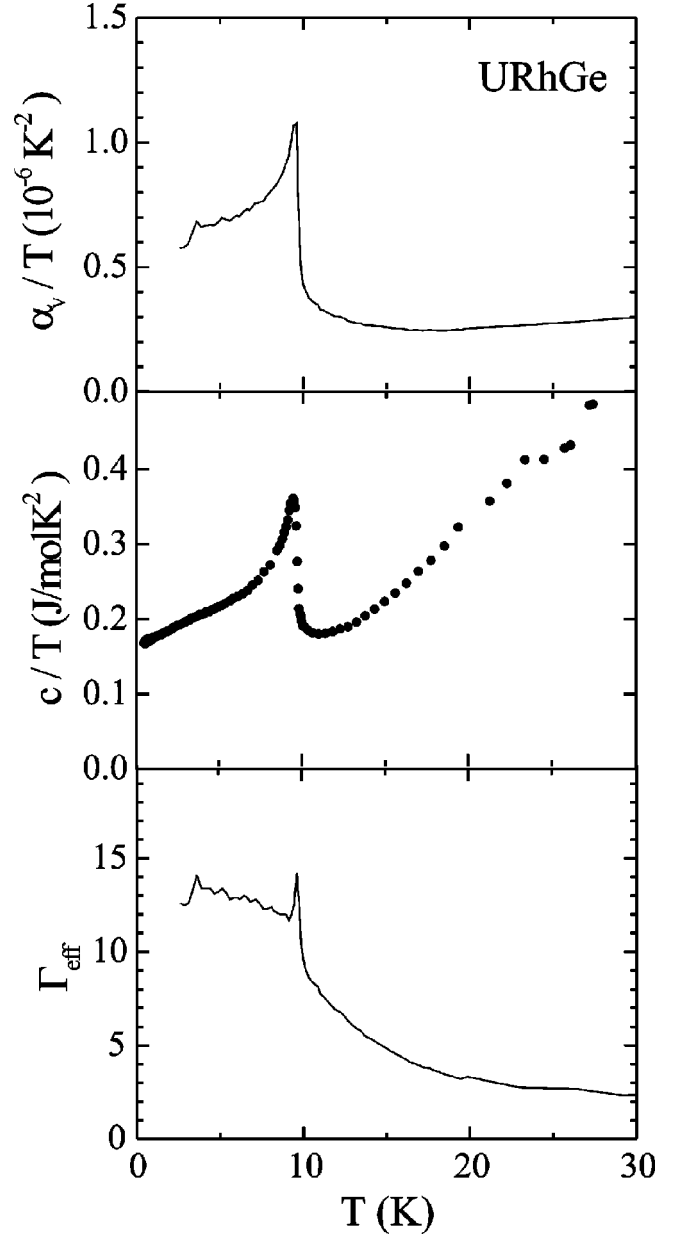

FIG. 3. The volume expansion divided by temperature (α_v/T) of URhGe as a function of temperature T at low temperatures. For comparison the specific heat divided by temperature (c/T), of a sample prepared from the same single-crystalline batch is shown.[13] The bottom frame shows the effective Grüneisen parameter Γ_{eff}, determined from the experimental data of the volume expansion and the specific heat (see text).

have applied the Ehrenfest relation. For a second-order phase transition, the uniaxial pressure dependence of the transition temperature is directly related to the step anomalies in the coefficient of linear thermal expansion and the specific heat by the Ehrenfest relation:

$$\frac{dT_C}{dp_i} = \frac{V_m \Delta \alpha_i}{\Delta(c/T)}, \tag{1}$$

where the index i refers to the orthorhombic axis, $V_m = 3.36 \times 10^{-5}$ m^3/mol is the molar volume and $\Delta(c/T)$

$=0.22(1)$ J/molK^2 is the anomaly in the specific heat divided by temperature.[12] By applying this relation to the experimental step anomalies in the coefficients of linear thermal expansion, the uniaxial pressure dependence of T_C along the a, b, and c axis is obtained. The calculated values are listed in Table I. The hydrostatic pressure dependence of T_C can be obtained by inserting the volume expansion for the coefficient of linear expansion in Eq. (1), or by summing the three contributions of the uniaxial pressure dependence. The different pressure dependencies of T_C as listed in Table I are all positive. This strongly suggests that the ferromagnetic order cannot be suppressed by moderate mechanical hydrostatic or uniaxial pressures, like in the case of UGe$_2$ and ZrZn$_2$. Instead a *negative* uniaxial pressure is needed to suppress T_C for all crystallographic directions. Using a simple linear extrapolation of the initial pressure dependence calculated from the Ehrenfest relation, we arrive at a negative critical hydrostatic pressure of $p_{cr} \approx -80$ kbar. It is important to note that this value should be regarded as an upper bound for the negative critical pressure as the pressure dependence of T_C is expected to show significant nonlinear corrections to the initial pressure dependence at ambient pressure. A negative critical pressure of the order of $p_{cr} \approx -80$ kbar might be achieved by suitable chemical substitutions.

In order to characterize the volume dependence of the electron correlations, we have calculated the effective Grüneisen parameter of URhGe. The effective Grüneisen parameter Γ_{eff} is calculated from the temperature-dependent volume expansion $\alpha_v(T)$ and specific heat $c(T)$:

$$\Gamma_{eff}(T) = \frac{V_m \alpha_v(T)}{\kappa c(T)}, \qquad (2)$$

where $\kappa = -(1/V)(dV/dp)$ is the isothermal compressibility. As the compressibility of URhGe is unknown we will use an estimated value $\kappa = 0.8$ Mbar^{-1}. Experimental values for the compressibility of other UTX compounds vary from $\kappa = 0.6$ to 1.0 Mbar^{-1} (Ref. 23). In Fig. 3 the effective Grüneisen parameter Γ_{eff}, calculated from the experimental volume expansion and the reported specific heat,[13] is shown as a function of temperature. At high temperatures the effective Grüneisen parameter shows a small constant value of $\Gamma_{ph} = 2$ and describes the volume dependence of the characteristic energy scale for the phonons. Below 30 K the effective Grüneisen parameter rapidly increases and reaches a value of $\Gamma_{eff} \approx 14$ just above T_C. Below T_C a weak suppression of the effective Grüneisen parameter is observed with a slow increase for decreasing temperatures. In the low-temperature limit Γ_{eff}

corresponds to the enhanced electronic Grüneisen parameter $\Gamma_{sf} = d \ln \gamma / d \ln V \approx 14$ of the ferromagnetic spin fluctuations. The corresponding relative pressure dependence of the electronic specific heat amounts to $d \ln \gamma / dp = -\kappa \Gamma_{sf} \approx -18$ Mbar^{-1}.

The relation between magnetic order and the spin fluctuations can further be studied by comparing the volume dependence of the energy scales for the ferromagnetic order (T_C) and the ferromagnetic spin fluctuations (T_{sf}). It turns out that the Grüneisen parameter for the ferromagnetic order $\Gamma_F = -d \ln T_C / d \ln V = (1/\kappa T_C)(dT_C/dp) \approx 16$ is of the same order of magnitude and has the same sign as the Grüneisen parameter for the ferromagnetic spin fluctuations $\Gamma_{sf} = -d \ln T_{sf} / d \ln V = d \ln \gamma / d \ln V \approx 14$. This situation is in strong contrast to pressure-induced antiferromagnetic superconductors such as CePd$_2$Si$_2$ (Ref. 24), where the antiferromagnetic order competes with the spin fluctuations with an opposite scaling behavior with volume. It can therefore be expected that the spin-mediated superconductivity of URhGe exists over a wide pressure range, as observed for the ferromagnetic superconductor ZrZn$_2$ (Ref. 3). This in contrast to the situation in the ferromagnetic superconductor UGe$_2$ (Ref. 2), where superconductivity is only observed in a small pressure region close to the critical pressure where the ferromagnetic order is suppressed.

V. CONCLUSIONS

We have performed thermal expansion measurements on a single-crystalline sample of the ferromagnet URhGe. Below the ferromagnetic ordering temperature of $T_C = 9.7$ K an increase in the coefficient of linear thermal expansion was observed along all three orthorhombic axes. The uniaxial pressure dependence of the ferromagnetic transition temperature was determined by the Ehrenfest relation from the anomalies in the coefficients of linear thermal expansion and the specific heat. We find positive values of dT_C/dp for all principal axes. Consequently, the hydrostatic pressure dependence is also positive and amounts to $dT_C/dp = 0.12$ K/kbar. This contrasts the behavior reported for UGe$_2$ and ZrZn$_2$. In addition, the effective Grüneisen parameter was determined. The resulting low-temperature behavior points to an enhanced volume dependence of the ferromagnetic spin fluctuations at low temperatures and an equal volume scaling of the energy scales for the ferromagnetic order and the ferromagnetic spin fluctuations.

*Email address: S.Sakarya@iri.tudelft.nl

[1] D. Aoki, A. Huxley, E. Ressouche, D. Braithwaite, J. Flouquet, J.-P. Brison, E. Lhotel, and C. Paulsen, Nature (London) **413**, 613 (2001).

[2] S.S. Saxena, P. Agarwal, K. Ahilan, F.M. Grosche, R.K.W. Hasselwimmer, M.J. Steiner, E. Pugh, I.R. Walker, S.R. Julian, P. Monthoux, G.G. Lonzarich, A. Huxley, I. Sheikin, D. Braith-

waite, and J. Flouquet, Nature (London) **406**, 587 (2000).

[3] C. Pfleiderer, M. Uhlarz, S.M. Hayden, R. Vollmer, H.v. Lohneysen, N.R. Bernhoeft, and G.G. Lonzarich, Nature (London) **412**, 58 (2001).

[4] W.A. Fertig, D.C. Johnston, L.E. DeLong, R.W. McCallum, M.B. Maple, and B.T. Matthias, Phys. Rev. Lett. **38**, 987 (1977).

[5] D.E. Moncton, D.B. McWhan, P.H. Schmidt, G. Shirane,

W. Thomlinson, M.B. Maple, H.B. MacKay, L.D. Woolf, Z. Fisk, and D.C. Johnston, Phys. Rev. Lett. **45**, 2060 (1980).

[6] M. Ishikawa and O. Fischer, Solid State Commun. **23**, 37 (1977).

[7] N.I. Karchev, K.B. Blagoev, K.S. Bedell, and P.B. Littlewood, Phys. Rev. Lett. **86**, 846 (2001).

[8] K. Machida and T. Ohmi, Phys. Rev. Lett. **86**, 850 (2001).

[9] T.R. Kirkpatrick, D. Belitz, T. Vojta, and R. Narayanan, Phys. Rev. Lett. **87**, 127003 (2001).

[10] H. Suhl, Phys. Rev. Lett. **87**, 167007 (2001).

[11] V. Sechovsky and L. Havela, in *Handbook of Magnetic Materials*, edited by K.H.J. Buschow (North-Holland, Amsterdam, 1998), Vol. 11, p. 1.

[12] K. Prokes, T. Tahara, Y. Echizen, T. Takabatake, T. Fujita, I.H. Hagmusa, J.C.P. Klaasse, E. Brück, F.R. de Boer, M. Divis, and V. Sechovsky, Physica B **311**, 220 (2002).

[13] I.H. Hagmusa, K. Prokes, Y. Echizen, T. Takabatake, T. Fujita, J.C.P. Klaasse, E. Bruck, V. Sechovsky, and F.R. de Boer, Physica B **281**, 223 (2000).

[14] V.H. Tran and R. Troc, Phys. Rev. B **57**, 11 592 (1998).

[15] V.H. Tran, R. Troc, and G. André, J. Magn. Magn. Mater. **186**, 81 (1998).

[16] F.R. de Boer, E. Bruck, V. Sechovsky, L. Havela, and K.H.J. Buschow, Physica B **163**, 175 (1990).

[17] K.H.J. Buschow, E. Brück, R.G. van Wierst, F.R. de Boer, L. Havela, V. Sechovsky, P. Nozar, E. Sugiura, M. Ono, M. Date, and A. Yamagishi, J. Appl. Phys. **67**, 5215 (1990).

[18] B. Chevalier, E. Hickey, and J. Etourneau, J. Magn. Magn. Mater. **90**, 499 (1990).

[19] R. Troc and V.H. Tran, J. Magn. Magn. Mater. **73**, 389 (1988).

[20] A.B. Shick, Phys. Rev. B **65**, 180509(R) (2002).

[21] M. Divis, L.M. Sandratskii, M. Richter, P. Mohn, and P. Novák, J. Alloys Compd. **337**, 48 (2002).

[22] A. de Visser, Ph.D. thesis, University of Amsterdam, 1986.

[23] L. Havela, M. Divis, V. Sechovsky, A. Andreev, F. Honda, G. Oomi, Y. Méresse, and S. Heathman, J. Alloys Compd. **322**, 7 (2001).

[24] N.H. van Dijk, B. Fak, T. Charvolin, P. Lejay, and J. Mignot, Phys. Rev. B **61**, 8922 (2000).