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SUPERCONDUCTIVITY AND MAGNETIC ORDERING IN THE MIXED TERNARY $Er_xY_{1-x}Rh_{1.1}Sn_{3.6}$ SYSTEM

E.P. HOUWMAN, A.W.M. VAN DE PASCH and J. FLOKSTRA
University of Twente, Department of Applied Physics, P.O. Box 217, 7500 AE Enschede, The Netherlands

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The superconducting transition temperature T_c as well as the magnetic ordering temperature T_m have been determined in the mixed ternary compound $Er_xY_{1-x}Rh_{1.1}Sn_{3.6}$ as a function of the Er concentration. T_c decreases from 3.13 K for $YRh_{1.1}Sn_{3.6}$ to 1.1 K for $ErRh_{1.1}Sn_{3.6}$. Reentrant superconductivity has been found for $x > 0.6$.

The application of the models of Abrikosov and Gorkov, Maekawa and Tachiki, and Roshen and Ruvalds to this system is discussed. T_c as function of the concentration x is best described by the model of Roshen and Ruvalds assuming a ferromagnetic interaction between the spins. The parameter $I^2N(0)$, arising from electron spin interaction, is found to be 0.088 K. The ferromagnetic ordering temperature dependence is described by the theory of Oguchi and Ono, using an effective coordination number $z = 6$ and an exchange constant of $J' = 0.30$ K.

1. Introduction

Since the discovery of ternary compounds like the Chevrel phases $RE_xMo_6S_8$ [1] and $RE_xMo_6Se_8$ [2] and the $RERh_4B_4$ series [3], which show for some of the rare-earth (RE) metals superconductivity as well as magnetic ordering, there is a growing interest in the study of the interaction between these phenomena. Mixed ternary systems, formed by alloying two members of a family of compounds, offer a possibility to investigate the competition between superconductivity and magnetism as a function of the concentration of magnetic moments. Many studies on this subject involved the Chevrel phases and the rhodium borides [4–7].

More recently a new family of superconducting or magnetically ordering ternary compounds, the rhodium stannides, has been found [8]. Although it appears to be relatively easy to prepare large single crystals, up till now only little has been published about the superconducting and magnetic properties of these compounds [9]. In this family of ternary compounds the $ErRh_{1.1}Sn_{3.6}$ shows reentrant superconductivity. The superconducting transition temperature T_c is reported to be about 1.2 K and the magnetic ordering temperature T_m is 0.6 K [8]. The other rhodium stannides show either superconductivity or magnetic ordering. $YRh_{1.1}Sn_{3.6}$ becomes superconducting below 3.2 K [8]. Lately the complex crystal structure of this compound has been solved [10].

In order to study the interplay between both ordering mechanisms, we made mixed crystals of $Er_xY_{1-x}Rh_{1.1}Sn_{3.6}$. The non-magnetic Y was chosen for mixing with Er, because they have almost the same ionic radius and their compounds have the same crystal structure and nearly equal lattice constants. Substitution of Y ions by Er ions will reduce the superconducting transition temperature and enables magnetic ordering at sufficiently high Er concentrations. Here we report on a study of the variation of T_c and T_m with concentration in the pseudo-ternary system $Er_xY_{1-x}Rh_{1.1}Sn_{3.6}$.

The discovery of magnetic superconductors has given rise to the development of several new theories for describing the influence of magnetic atoms on the superconducting and magnetic properties of these compounds. Most of these theories start with a citation of the theory of Abrikosov and Gorkov (AG) [11], that describes the influence of scattering of electrons by isolated spins on the superconducting transition temperature. For low concentration of paramag-

netic atoms in a superconducting compound this results in a linear depression of T_c with increasing concentration. This has been confirmed by many experiments [4, 6] and therefore the AG-theory has set a standard for theory in the low-concentration region. At higher concentrations spin correlation effects will become of importance.

Roshen and Ruvalds (RR) [12] extended the AG-theory by taking into account the influence of the formation of coupled spin pairs on the electron scattering rate and thus on the reduction of the superconducting transition temperature. Parallel coupling of the spins causes an extra reduction of T_c and for high concentration of magnetic atoms also reentrant behaviour, whereas antiparallel coupling enhances superconductivity. We found that, assuming a spin–spin interaction that favours a parallel alignment of spins, this theory gives a fairly good description of the superconducting transition temperatures as function of the concentration of Er atoms in the $Er_xY_{1-x}Rh_{1.1}Sn_{3.6}$ mixed system.

The extreme of high concentration of magnetic atoms may be described by a model of Maekawa and Tachiki (MT) [13]. They assume that short-range ordering of the spins arises at temperatures above the actual ordering temperature. Inelastic scattering of the electrons by fluctuations of the ordered spin system destroys superconductivity and causes reentrant behavior in ferromagnetic superconductors. For describing the magnetic ordering use is made of a model of Oguchi and Ono (OO) [14]. The MT-model will fail at low concentrations. Its application to the $Er_xY_{1-x}Rh_{1.1}Sn_{3.6}$ system will be discussed.

2. Experimental results

For the preparation of the compounds $Er_xY_{1-x}Rh_{1.1}Sn_{3.6}$ we used the recipe of Espinosa [8, 15], which gives crystals with a tetragonal structure known as phase II [10], by adding the Er and Y in the aimed ratio of atomic concentrations and the Er + Y and Rh in the ratio 1 to 2 to the melt. We prepared crystals with expected concentrations of $x = 0$, 0.2, 0.4, 0.5, 0.6, 0.8, 0.9 and 1. The crystallographic structure of some crystals of this series was checked by means of X-ray diffraction. We found in all cases the phase II structure, but the tetragonal axis appeared in three directions perpendicular to each other as mentioned in literature [10].

The Er concentration in the crystals was determined by comparing the measured paramagnetic susceptibility of the mixed crystals to that of $ErRh_{1.1}Sn_{3.6}$. For some of the crystals we had to correct for the influence of small inclusions of pure Sn. The concentrations found in this way did not differ more than about $\Delta x = 0.02$ from the expected values.

All transition temperatures above 1.2 K were determined by measuring the ac-susceptibility with decreasing temperature of the liquid-helium bath using our mutual inductance SQUID-susceptometer at a frequency of 80 Hz and an rms-value of the ac-field down to 0.2 μT [16]. Measurements for $T < 1.2$ K were performed in a ^3He–^4He dilution refrigerator by measuring the dc-magnetization with a SQUID-magnetometer in a small background field [17].

A typical ac-susceptibility measurement of the normal-to-superconducting transition is shown for a crystal of $Er_{0.4}Y_{0.6}Rh_{1.1}Sn_{3.6}$ in fig. 1. The susceptibility starts at its paramagnetic value and

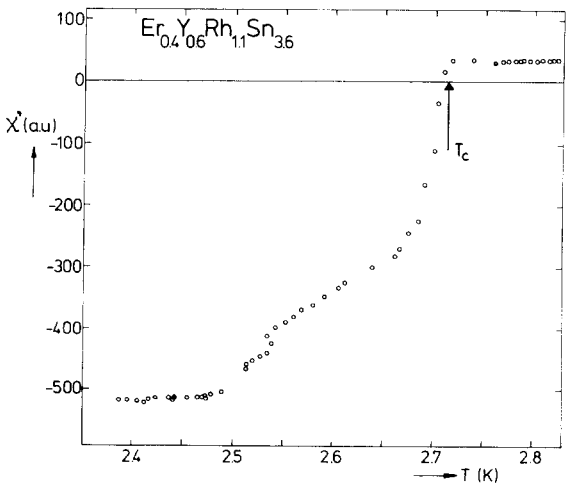

Fig. 1. The ac-susceptibility of a crystal of $Er_{0.4}Y_{0.6}Rh_{1.1}Sn_{3.6}$ in the transition temperature region, with an oscillating field $\mu_0 h_{ac} = 0.3$ μT. The external field is zero.

reaches the value $-(1-D)^{-1}$, representing a complete screening of the sample for the oscillating field, D being an effective demagnetizing factor. The transition region exhibits a sharp decrease followed by a shoulder in the low-temperature part of the transition. It is found that the susceptibility in the transition region is dependent on the amplitude of the oscillating field and therefore we present the final value of the susceptibility for small amplitude, which appears to be isothermal for almost the whole transition temperature range. The width of the transition varies from sample to sample and has values between 0.1 K and 0.35 K. In some of the crystals no shoulder was found. We define the superconducting transition temperature T_c as that temperature, where the ac-susceptibility starts to deviate from the Curie–Weiss law at decreasing temperature in the small amplitude limit. The experimental values of T_c are presented in figs. 3 and 4 to facilitate comparison with different theories.

The superconducting transition temperatures of the compounds with $x = 0.8$, 0.9, 1, and the magnetic ordering temperatures were measured in the dilution refrigerator. Fig. 2 shows a typical measurement of the dc-magnetization of $ErRh_{1.1}Sn_{3.6}$ with varying temperature in a small background field of about 60 μT. The many details of the curves will be discussed elsewhere. Here we restrict ourselves to the determination of T_c, taken from the point where the magnetization starts to deviate from that according to the Curie–Weiss law, and of T_m, derived from the sharp rise of the magnetization when it goes from the value at the superconducting state to that of a ferromagnet. The results are also presented in figs. 3 and 4.

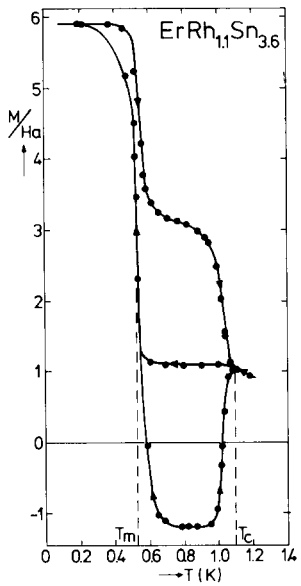

Fig. 2. The dc-magnetization of a crystal of $Er\,Rh_{1.1}Sn_{3.6}$ vs. temperature in units of the applied field $\mu_0 H_a = 60\ \mu T$. The superconducting and magnetic transition temperature are indicated.

3. Theory, application and discussion

The decrease of the transition temperature of superconductors with low concentrations of paramagnetic ions is usually explained by the theory of Abrikosov and Gorkov [11]. In this model the effect of spin-flip scattering of the conduction electrons due to the exchange interaction between the spin s of an electron and the spin S of a magnetic ion is considered. It is assumed that the localized spins have no interaction with each other for all concentrations.

The variation of the superconducting transition temperature T_c with the relative concentration x of the paramagnetic ions is given by

$$\ln\left(\frac{T_{co}}{T_c}\right) = \Psi(\tfrac{1}{2}+\rho) - \Psi(\tfrac{1}{2}),$$
$$\rho = 1/2\pi T_c \tau_{AG}, \qquad (1)$$
$$1/\tau_{AG} = 2\pi I^2 N(0) G x,$$

taking h and k_B equal to 1 for simplicity. Ψ is the digamma function and T_{co} the transition temperature of the pure superconductor. The Cooper pair breaking function ρ is determined by the scattering rate $1/\tau_{AG}$, due to the spin–electron interaction $Is \cdot S$ and by T_c. $N(0)$ is the density of states at the Fermi level and the De Gennes factor G is given by $G = (g_J - 1)^2 \times J(J+1)$, where g_J is the Landé factor and J the total angular momentum. For $\rho \ll \frac{1}{2}$, eq. (1)

reduces to a linear decrease of T_c with the concentration:

$$\frac{dT_c}{dx} = -\frac{\pi^2}{2} I^2 N(0) G , \tag{2}$$

offering the possibility to determine the parameter $I^2N(0)$ from the slope of the experimental $T_c(x)$ curve for low concentrations.

We applied the AG-theory to $Er_xY_{1-x}Rh_{1.1}Sn_{3.6}$ by taking $J = 15/2$ and $G = 2.55$ for the Er^{3+} ion and $T_{co} = 3.13$ K, as was found from our experiments. From a fit to the data points for $x \leq 0.4$ in fig. 3, we found $I^2N(0) = 0.088$ K. Using these parameters, T_c was calculated as function of x from eq. (1) and the results are depicted as the dashed curve in figs. 3 and 4. For $x \leq 0.4$ the AG-theory describes the reduction of T_c as function of the concentrations of Er-atoms fairly well, but for larger concentrations T_c is reduced more than can be explained by the AG-theory.

Several mechanisms have been proposed to explain the reduction of T_c for large concentrations of magnetic atoms. We will discuss two models and apply them to the $Er_xY_{1-x}Rh_{1.1}Sn_{3.6}$ system.

For large concentrations of magnetic atoms it is generally not legitimate to neglect the interaction between the localized magnetic moments as is done in the AG-theory. Maekawa and Tachiki [13] consider a magnetic superconductor in which the interaction between the spins of the magnetic atoms gives rise to short-range ordering above the magnetic ordering temperature T_m. Inelastic scattering of the conductions electrons by fluctuations of the spin system leads to pair breaking and thus to a reduction of T_c. Scattering by isolated spins is neglected and therefore the model will not be applicable for low concentrations of magnetic ions.

MT arrive at the following expression for $T_c(x)$,

$$T_c(x) = 1.13\,\omega_D \exp\left\{-1\Big/\left[g_{BCS}N(0) - \frac{x' I^2 N(0) G}{4k_F^2 D} \ln\left(1 + \frac{4k_F^2 D}{T_c(x) - T_m}\right)\right]\right\} , \tag{3}$$

where ω_D is the Debije energy, g_{BCS} the phonon-mediated electron–electron interaction constant from the BCS-theory and k_F the Fermi wave vector in units of the inverse of a specific lattice constant a. T_m and D are functions of $T_c(x)$ and follow from the spin susceptibility given below. It is seen from eq. (3) that the attractive electron–electron interaction is reduced by the interaction of the electrons with the spin fluctuations.

From our measurements it follows that for $x = 0.8$, 0.9 and 1.0 $Er_xY_{1-x}Rh_{1.1}Sn_{3.6}$ behaves as a reentrant superconductor and therefore we describe the spin susceptibility of this system by that of a ferromagnet. In ferromagnets ordering with a single wave vector $q = 0$ can occur. In that case spin fluctuations with small wave vector will dominate just above T_m. Oguchi and Ono [14] derived an expression for the spin susceptibility of an isotropic Heisenberg system, taking into account only nearest neighbour interaction. The dependence on the concentration of magnetic ions is also included:

$$\chi(q) = \frac{\frac{1}{3}x'G}{T - T_m(T, x) + D(T, x)q^2} , \tag{4a}$$

$$T_m(T, x) = \tfrac{1}{4} z' T (1 - \exp(-2J'/T)) , \tag{4b}$$

$$D(T, x) = \frac{z' + 1}{z'} \times \frac{T}{2}\left(1 - \frac{T}{2J'}(1 - \exp(-2J'/T))\right) . \tag{4c}$$

J' is the nearest neighbour interaction constant, z' is the number of nearest neighbour spins $z' = 1 + (z - 1)x'$, where z is the coordination number in the non-diluted case, and x' the concentration of non-isolated spins: $x' = x(1 - (1 - x)^z)$. The magnetic ordering temperature of a magnetically diluted system follows directly from eq. (4b):

$$J'/T_m = \tfrac{1}{2} \ln\left(\frac{z'}{z' - 4}\right) . \tag{5}$$

In order to apply the MT-model to the system $Er_xY_{1-x}Rh_{1.1}Sn_{3.6}$ values are needed for the parameters ω_D, $g_{BCS}N(0)$, z, J' and k_F apart

from T_{co} and $I^2N(0)G$ which were determined earlier. Taking the usual value $g_{BCS}N(0) = 0.3$, ω_D is fixed. Because of the complicated structure of the Er-sublattice [10] there is not a well defined coordination number z. We defined an effective number z_{eff} based on the consideration that eq. (5) implies a critical concentration completely determined by z, below which no magnetic ordering appears. Because no ordering was found for $x \leq 0.6$, we used $z_{eff} = 6$. Together with the magnetic ordering temperature for $x = 1$, $T_m(x = 1) = 0.55$ K, J' was calculated as $J' = 0.30$ K. The theoretical dependence of T_m on x was calculated with eq. (5) and the curve is shown in figs. 3 and 4, indicated by OO. The measured $T_c(x)$ values fit the best to a theoretical curve according to eq. (3) with a scaled wave vector $k_F = 4.2$. This implies that k_F has the reasonable value of about 1.4 Å^{-1}, using a nearest neighbour distance of 3 Å as the specific lattice constant.

It is seen from fig. 3 that the theoretical MT-curve describes the observed normal to superconducting transition temperature as function of the concentration of Er atoms fairly well for $x > 0.5$. At the low concentration side the MT-theory predicts too little reduction of T_c. This is not surprising because the elastic scattering from isolated spins is neglected and collective spin fluctuations only lead to a weak scattering potential at low concentrations.

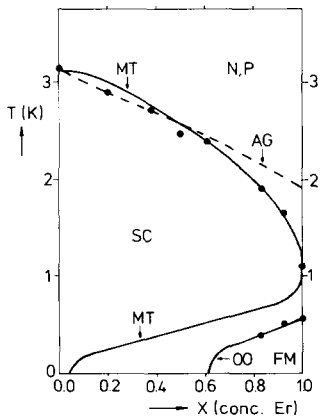

Fig. 3. Comparison of the experimental T_c and T_m values with the theories of AG, MT and OO. N,P = normal paramagnetic; SC = superconducting; FM = ferromagnetic.

Apart from the poor agreement in the low concentration region and despite of the fact that the MT-theory describes the experimental $T_c(x)$ curve well for $x > 0.5$, there can be made some further objections to the application of this theory to the $Er_xY_{1-x}Rh_{1.1}Sn_{3.6}$ system. The model implicitly assumes the occurrence of long range ordering below T_m and predicts a return to the normal state for most concentrations at decreasing temperature as can be seen from fig. 3. In the high concentration range an intermediate normal state should appear before the system orders ferromagnetically. Experimentally there has been found no evidence for the occurrence of the normal state for $x < 0.6$ and the intermediate state for $x > 0.6$.

Furthermore, neutron diffraction measurements indicate that no true long range ordering appears below T_m [18]. This may be attributed to the complex structure of the magnetic sublattice which might favour ordering in small clusters. Hence spin correlation over larger distances is not very plausible for $T > T_m$.

From the above considerations we concluded that the model of MT is not very suitable to describe the phase diagram of the $Er_xY_{1-x}Rh_{1.1}Sn_{3.6}$ system.

We now turn to the application of the model of Roshen and Ruvalds [12], which is an extension of the AG-theory. Apart from the elastic scattering by isolated spins also the elastic scattering of conduction electrons by coupled spin pairs is taken into account. The scattering rate $1/\tau_{sp}$ arising from these coupled spins was calculated for nearest neighbour spins only, assuming a conduction electron mediated spin–spin interaction (RKKY-interaction). The total scattering rate is given by

$$\frac{1}{\tau} = \frac{1}{\tau_{AG}} + \frac{1}{\tau_{sp}},$$
$$\frac{1}{\tau_{sp}} = -4\pi I^2 N(0) \frac{G^2}{3} \frac{1}{T} U_{RKKY} A\dot{z}x^2, \qquad (6)$$

where U_{RKKY} is the RKKY-interaction potential and A a phase factor, both given in ref. [12]. The most important feature of $1/\tau_{sp}$ is the $1/T$ divergence, which leads to reentrant behaviour at low

temperatures in case of ferromagnetic coupling. This feature is retained for other types of spin–spin interaction. The total scattering rate can be written as

$$\frac{1}{\tau} = \frac{1}{\tau_{AG}}\left(1 + \alpha \frac{x}{T}\right), \tag{7}$$

where $\alpha = -2GU_{RKKY}Az/3$.

Using $1/\tau$ instead of $1/\tau_{AG}$ in eq. (1), we calculated the concentration dependent transition temperature. A value of 0.64 K for α was found by fitting $T_c(x = 1)$ to the measured transition temperature. The $T_c(x)$ curve, calculated with this α, is shown in fig. 4. It is seen that the RR-model describes the experimental data for high temperatures very well over the whole concentration range. Comparison with the AG-curve shows that scattering by coupled spin pairs gives a significant extra reduction of T_c at high concentrations. The low-temperature transition to the normal state, which is predicted by the RR-theory, does not correspond to the measurements. This will be due to the fact that the model only considers scattering from isolated spins and nearest neighbour spin pairs, whereas at low temperatures also scattering from larger spin clusters will become important.

For the system under consideration the model of Roshen and Ruvalds gives a good description of the T_c versus x relation. The spin–spin interaction is apparently weak enough for all concentrations to consider the scattering by spin pairs as a first-order correction on the scattering by isolated spins. In contrast with the MT-model, the RR-model can be used for the whole concentration range. The transition to the ferromagnetic ordered state is described also in this case by the OO-theory.

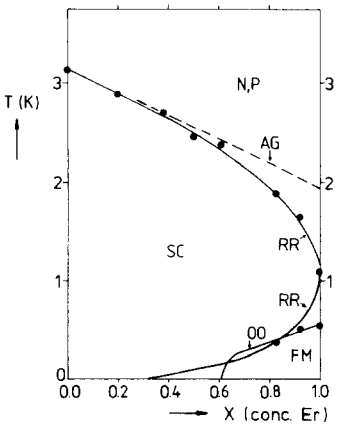

Fig. 4. Comparison of the experimental T_c and T_m values with the theories of AG, RR and OO. See also fig. 3.

4. Conclusions

We determined the phase diagram of the superconducting and ferromagnetic ordering temperature versus concentration in the mixed ternary compound $Er_xY_{1-x}Rh_{1.1}Sn_{3.6}$. Substitution of Y by Er suppresses the superconducting transition temperature. For $x \leq 0.4$ this suppression can be described by the theory of Abrikosov and Gorkov, considering elastic scattering of conduction electrons by isolated spins, using $I^2N(0) = 0.088$ K. For larger Er concentrations T_c is reduced more than predicted by the AG-theory. This extra reduction is attributed to an additional scattering rate, due to parallel alignment of nearest neighbour spins in coupled spin pairs, which is proportional to x^2/T as is described in the model of Roshen and Ruvalds. The model of Maekawa and Tachiki, in which the conduction electrons are scattered inelastically by collective spin fluctuations, appears to be not applicable to this system. The magnetic ordering temperature as function of the concentration is described fairly well by the model of Oguchi and Ono, with an effective coordination number $z_{eff} = 6$ and an exchange constant $J' = 0.30$ K.

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References

[1] Ø. Fischer, A. Treyvaud, R. Chevrel and M. Sergent, Solid State Comun. 17 (1975) 721.
[2] R.N. Shelton, R.W. McCallum and H. Adrian, Phys. Lett. A 56 (1976) 213.

[3] B.T. Matthias, E. Corenzwit, J.M. Vandenberg and H. Barz, Proc. Nat. Ac. Sci. USA 74 (1977) 1334.
[4] S.E. Lambert, M.B. Maple and B.D. Dunlap, Phys. Rev. B 33 (1986) 3129.
[5] K. Okuda, Y. Nakakura and K. Kadowaki, Solid. State Commun. 32 (1979) 185.
[6] H. Adrian, R. Müller, R. Behrle, G. Saemann-Ischenko and G. Voit, Physica 108B (1981) 1281.
[7] M. Ishikawa, M. Sergent and Ø. Fischer, Phys. Lett. A 82 (1981) 30.
[8] J.P. Remeika, G.P. Espinosa, A.S. Cooper, H. Barz, J.M. Rowell, D.W. McWhan, J.M. Vandenberg, D.E. Moncton, Z. Fisk, L.D. Woolf, H.C. Hamaker, M.B. Maple, G. Shirane and W. Thomlinson, Solid State Commun. 34 (1980) 923.
[9] K. Andres, J.P. Remeika, G.P. Espinosa and A.S. Cooper, Phys. Rev. B 23 (1981) 1179.
[10] J.L. Hodeau, M. Marezio and J.P. Remeika, Acta. Cryst. B 40 (1984) 26.
[11] A.A. Abrikosov and L.P. Gorkov, Sov. Phys. JETP 12 (1984) 1243.
[12] W.A. Roshen and J. Ruvalds, Phys. Rev. B 31 (1985) 2929.
[13] S. Maekawa and M. Tachiki, Phys. Rev. B 18 (1978) 4688.
[14] T. Oguchi and I. Ono, J. Phys. Soc. Japan 21 (1966) 2178.
[15] G.P. Espinosa, Mat. Res. Bull. 15 (1980) 791.
[16] J.A. Overweg, H.J.M. ter Brake, J. Flokstra and G.J. Gerritsma, J. Phys. E 16 (1983) 1247.
[17] D.H.A. Blank, H.J.M. ter Brake and J. Flokstra, Proc. IC-SQUID '85 (De Gruyter, Berlin, 1985), p. 859.
[18] J.L. Hodeau, P. Bordet, P. Wolfers, M. Marezio and J.P. Remeika, J. Magn. Magn. Mat. 54–57 (1986) 1527.