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Superconductivity and Magnetism of $Dy_{1-x}Y_xRh_4B_4$: Candidate for Spin–Triplet Cooper Pairing

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In this work for the first time we give the evidence that compound $Dy_{1-x}Y_xRh_4B_4$ with the tetragonal body-centered crystal structure $LuRu_4B_4$ is the ferrimagnetic at temperatures $T_{\mathrm{Cur}} < 40$ K, ferrimagnetic superconductor at $T_{\mathrm{C}} < 10$ K and antiferromagnetic superconductor at $T_{\mathrm{N}} < 3$ K. No reentrant behavior was found down to $T = 0.32$ K. For the first time by means of a method of microcontact spectroscopy of the Andreev reflection in point contact Ag–$Dy_{0.8}Y_{0.2}Rh_4B_4$ the value and temperature and field dependences of superconducting gap parameter $\Delta(T,H)$ in $Dy_{0.8}Y_{0.2}Rh_4B_4$ were determined. The value of the ratio $2\Delta(0)/kT_{\mathrm{C}}$ is about 4. Some unusual features of $\Delta(T,H)$ dependences were observed, which give the evidence that the $Dy_{1-x}Y_xRh_4B_4$ is a candidate for spin–triplet Cooper pairing of charges with the parallel spins.

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1. Introduction

The problem of coexistence of superconductivity and magnetism as competing processes of ordering, has arisen fifty years ago and today has not lost its

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interest. The evidence for that are the studies in which it was shown that in compound Sr_2RuO_4 the electrons with parallel spins possess the superconducting pairing, forming a spin triplet or the odd coupled state. Unfortunately, Sr_2RuO_4 has low critical temperature T_C, near 1 K. In this connection, search of the different systems possessing similar properties at higher temperatures is very important.

Significant, and apparently the first, experimental works on this problem have been made in 1958 and presented in few papers, which have followed one after another [1, 2]. In them the important role of a spin subsystem in the organization of a superconducting pairing in magnetic superconductors has been found out (instead of the effective magnetic moments of the rare-earth elements).

In 1977 a number of compounds with chemical formula MRh_4B_4, where M = Y, Th or the rare-earth elements have been synthesized [3]. The part of these compounds has appeared to be superconducting, and other were ferromagnets. Rare-earth ions in these compounds formed ordered sublattice in perovskite crystal structures of $CeCo_4B_4$- and $LuRu_4B_4$-type, that provided long-range magnetic order. The information about mentioned crystal structures can be found in [3].

Compounds of MRh_4B_4-type possess remarkable property of creation of pseudo-ternary compounds due to solution of both Rh and the rare earth itself. It is the important tool of research of both — the basic properties, and interaction of superconductivity and the long-range magnetic ordering. The yttrium is the most suitable element for such attempts.

The important role in realization of unique superconducting and magnetic properties of pseudo-ternary compounds belongs to crystal structure and the stoichiometry. In the paper [4] the pseudo-ternary superconducting system of $Dy_{1-x}Y_xRh_4B_4$ with $LuRu_4B_4$ type of crystal structure has been synthesized and the interesting preliminary results were obtained.

The purpose of the present work was to find out on which magnetic background in system $Dy_{1-x}Y_xRh_4B_4$ with the body-centered tetragonal crystal structure of $LuRu_4B_4$-type a superconducting order arises; how the properties of system depends on its composition; what the basic superconducting parameters are and whether there are any preconditions for occurrence of triplet superconducting pairing.

2. Experimental results and discussion

Polycrystalline samples under study were prepared as was mentioned in [4]. The X-ray, electron-diffraction and optical analyses show that investigated samples were single-phased conglomerates of strongly alloyed (without intermediate inclusions and precipitations) crystallites with distinct single crystal faceting and $LuRu_4B_4$ crystal structure. Sizes of crystallites vary within 3–10 μm. Sizes of measured samples vary between $2 \times 2 \times 1$ mm^3 for point contact (PC) measurements and $1 \times 1 \times 5$ mm^3 for resistivity measurements. As experimental setups we used standard four-probe automatic measurement system, Quantum Design

SQUID magnetometer system, commercial Quantum Design PPMS, home made calorimeter with a thermal relaxation technique, home made system for PC measurements. For given composition, that is x, in the $Dy_{1-x}Y_xRh_4B_4$ system in all cases of measurements the meanings of the critical temperature T_C were within 5%. It says about high quality of our samples.

In Fig. 1 the results of magnetic measurements which show that all samples at temperatures above the critical temperature T_C are ferrimagnetics, except YRh_4B_4 (which is a paramagnetic) are presented. The measurements were made in zero field cooling (ZFC) regime in the magnetic field of 20 Oe. The obtained results represent so-called unusual dependences of $M(T)$ both in the region of magnetic ordering and in paramagnetic region of temperatures.

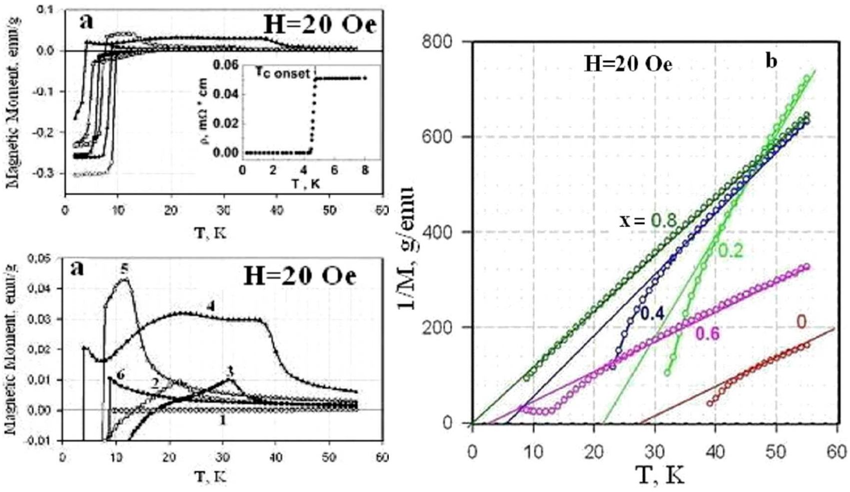

Fig. 1. Temperature dependence of magnetization (a) and its reciprocal value (which is proportional to reciprocal magnetic susceptibility $\chi^{-1}(T)$) (b). 1 — YR_4B_4; 2 — $Dy_{0.6}Y_{0.4}Rh_4B_4$; 3 — $Dy_{0.8}Y_{0.2}Rh_4B_4$; 4 — $DyRh_4B_4$; 5 — $Dy_{0.4}Y_{0.6}Rh_4B_4$; 6 — $Dy_{0.2}Y_{0.8}Rh_4B_4$. Inset in Fig. 1a shows the resistivity superconducting transition for $DyRh_4B_4$ with $T_C^{\mathrm{onset}} \approx 4.7$ K.

The theory and classification of such dependences for the first time have been introduced by Néel [5]. The physical meaning of such dependences is connected with the presence in compound at least two magnetic sublattices whose magnetic moments have opposite directions, are not always compensated, have various temperature dependences and are susceptible to formation of noncollinear magnetic structures. Such type of magnetism is known as uncompensated antiferromagnetism or ferrimagnetism as it is typical of a various types of ferrites.

It is seen that for various x the basic features of ferrimagnetic behavior of samples are found out: temperature dependence of reciprocal magnetic susceptibility $\chi^{-1}(T)$ at temperatures above the Curie temperature T_{Cur} is hyperbolic;

temperature dependences of spontaneous magnetization $M(T)$ at temperatures lower than T_{Cur} are of P and N types (according to classification of Néel [5, 6]); absence of saturation of $M(T)$ and presence of points of magnetic compensation at temperature T_{COM} (see curves 2 and 3 in Fig. 1a). The latter is the important result of the theory of ferrimagnetism. It is necessary to mention that the temperature T_{COM} is not the phase transition point. This is the point at which the opposite directed magnetizations of two sublattices become equal when temperature is decreasing. This happened because the values of these moments smoothly depend on temperature.

Another basic qualitative result of Néel's theory for paramagnetic region is the hyperbolic, instead of linear, dependence of reciprocal paramagnetic susceptibility on temperature which in this case is described by expression

$$\chi^{-1} = T/C + \chi_0^{-1} - \sigma/(T - T_{\mathrm{Cur}}), \quad (1)$$

where χ_0^{-1}, σ — complex functions of parameters of exchange interactions, C is a constant. The formula (1) considerably differs from the usual Curie–Weiss formula $\chi = C/(T - T_{\mathrm{Cur}})$ for ferromagnets by presence of last term. Just due to this term the temperature dependence of $\chi^{-1}(T)$ changes from linear to hyperbolic. The physical mechanism of sharp reduction of $\chi^{-1}(T)$ value near T_{Cur} remains unknown and up to now was not studied in detail. In work [7] it is supposed that occurrence of a hyperbolic temperature dependence of $\chi^{-1}(T)$ at $T > T_{\mathrm{Cur}}$ is caused by the influence of the one-directional exchange anisotropy. Just such physical meaning is possible to be ascribed to last term in expression (1). It is connected with that, as at temperatures above T_{Cur} the magnetic sublattices still exist. One of them, A (magnetic moment is along the magnetic field), is "strong" and another, B (magnetic moment is in opposite direction), is "weak". In process of temperature increasing the situation equalizes, the energy of the one-directional exchange anisotropy decreases and the value of $\chi^{-1}(T)$ changes to that what is described by the Curie–Weiss law. Let us pay attention to a curve with $x = 0.6$ in Fig. 1b which corresponds to sample $Dy_{0.4}Y_{0.6}Rh_4B_4$. It differs from others because at $T < 20$ K on a ferrimagnetic curve there is an opposite process. Earlier the same dependence of $\chi^{-1}(T)$ was observed in ferrite $Mn_3Fe_2Ge_3O_{12}$, and the idea of influence of complex exchange interaction was introduced [8]. The temperature of ferrimagnetic ordering T_{Cur} depends on x and with its increase decreases from $T_{\mathrm{Cur}} \approx 37$ K at $x = 0$ to $T_{\mathrm{Cur}} \approx 7$ K at $x = 0.8$.

It is also seen that substitution of Dy by Y not simply reduces T_{Cur}, but essentially influences the ferrimagnetic structure. As mentioned above, curves 2 and 3 demonstrate the presence of magnetic compensation points. The temperature of these points depend on sample composition and is $T_{\mathrm{COM}} \approx 14$ K for $Dy_{0.6}Y_{0.4}Rh_4B_4$ and $T_{\mathrm{COM}} \approx 18$ K — for $Dy_{0.8}Y_{0.2}Rh_4B_4$. Curve 4 has a flat part within the temperature interval 38–20 K, which may indicate that $DyRh_4B_4$ is a noncollinear ferrimagnetic. In this case in some interval of temperatures below T_{Cur} the resulting magnetization of ferrite does not depend on temperature and looks like $M = H/I_{AB}$, where H — a magnetic field, I_{AB} — a constant of exchange interaction between sublattices. The minimum at temperature near 8 K may say about the influence of the one-directional exchange anisotropy and the temperature of this minimum may be of so-called — low temperature Curie point.

It is seen from Fig. 1 that various samples have the transition into superconducting state at various signs and values of magnetization $M_{SC}(x)$. In Fig. 2 concentration dependences of $M_{SC}(x)$ and corresponding superconducting temperature T_C are presented. Practically linear dependence of T_C does not correlate with dependence of $M_{SC}(x)$, which changes sign and reaches the highest value at $x \approx 0.6$, exceeding $M_{SC}(x)$ value for $DyRh_4B_4$ approximately 1.7 times. It is only possible if non-magnetic yttrium goes into a weak sublattice, reducing its compensating influence on a strong sublattice.

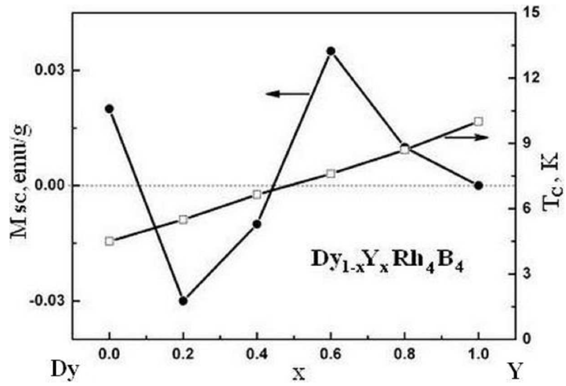

Fig. 2. The dependences of M_{SC} and T_C on the yttrium content x.

Therefore, the change of T_C seems to be correlated with the spin value of the system but not with the magnetic moment.

The heat capacity temperature dependences for some samples is presented in Fig. 3a. It is seen that YRh_4B_4 exhibits superconducting phase transition only. Samples with dysprosium besides superconducting phase transitions have ferrimagnetic-antiferromagnetic (AFM) phase transitions at temperatures T_{AFM}. The latter transitions are more pronounced. Dysprosium content more affects T_C than T_{AFM}. As follows from Fig. 3, ferrimagnetic–antiferromagnetic phase transitions (AFM) (a) in superconducting samples $DyRh_4B_4$ and $Dy_{0.8}Y_{0.2}Rh_4B_4$ at temperatures near $T_{AFM} \approx 3$ K essentially influence the temperature dependence of upper critical magnetic field H_{C2} (b) (see also [9]). The same is for $Dy_{0.7}Y_{0.3}Rh_4B_4$ sample.

By means of method of the Andreev reflection spectroscopy in point contact Ag–$Dy_{0.8}Y_{0.2}Rh_4B_4$ the differential resistances $dV/dI(V)(T,H)$ were measured and value and temperature and field dependences of superconducting gap parameter $\Delta(T,H)$ in $Dy_{0.8}Y_{0.2}Rh_4B_4$ were determined. The results are presented in Fig. 4.

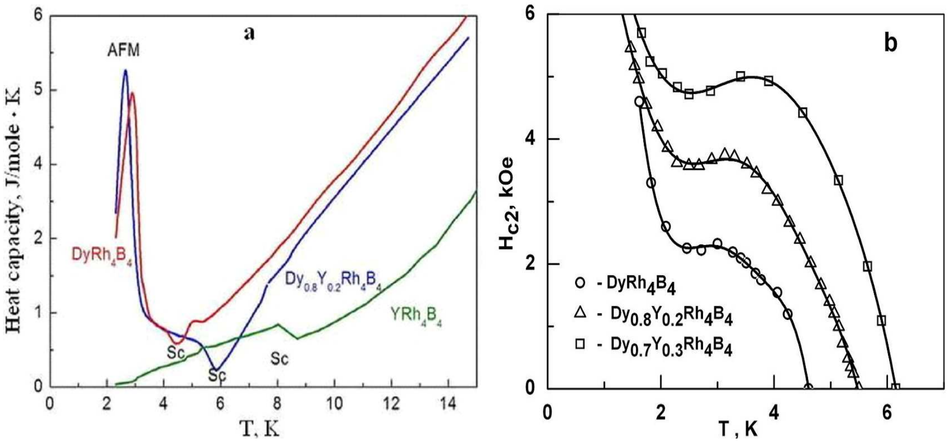

Fig. 3. Temperature dependence of the heat capacity (a) and upper critical magnetic field H_{C2} (b) for some compounds.

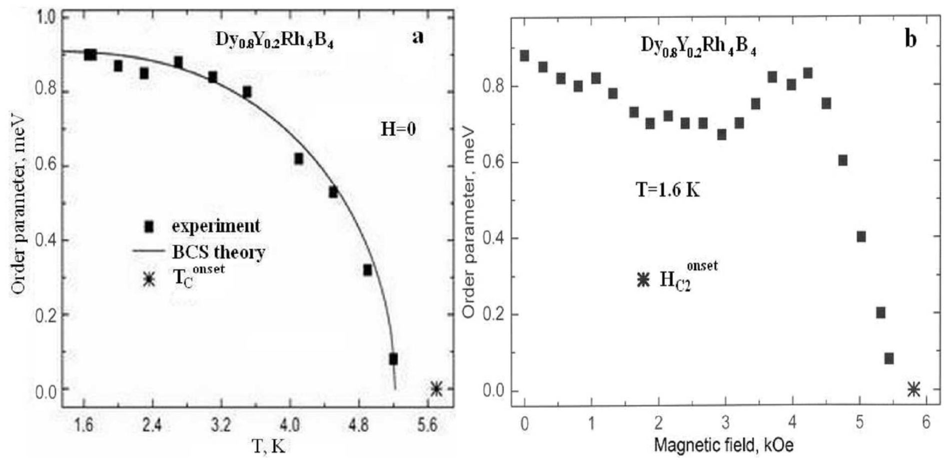

Fig. 4. Order parameter Δ for $Dy_{0.8}Y_{0.2}Rh_4B_4$ sample: temperature dependence of $\Delta(T)$ (a), magnetic field dependence of $\Delta(H)$ (b).

It is seen from Fig. 4a that within the temperature interval $T_C{-}T_{AFM}$ where the sample is in the ferrimagnetic state, the $\Delta(T)$ dependence follows the BCS theory. But at temperatures lower than T_{AFM} $\Delta(T)$ decreases instead of increasing due to the compensation of the magnetic moments. It may mean that for $T > T_{AFM}$ magnetic moments play important positive role in the creating of the superconducting state. From Fig. 4b we see that $\Delta(H)$ dependence is taken at temperature $T = 1.6$ K when the sample is in the antiferromagnetic state. When magnetic field increases up to 2 kOe, $\Delta(H)$ as usual goes down. But then this decrease in $\Delta(H)$ becomes slower and $\Delta(H)$ goes up at fields higher than 3 kOe. We suppose that magnetic fields higher than 2 kOe at this temperature destroy the

AFM state, restore uncompensated magnetic moment and superconducting order parameter grows up. Magnetic fields higher than 4 kOe destroy the superconducting state. Therefore, we see that intrinsic magnetism plays essential positive role in superconductivity of the investigated samples.

On the present stage of investigations we have some not answered questions: 1. Is there any difference between the states of superconductivity at temperatures lower and above T_{AFM}? May be that superconductivity at $T < T_{\mathrm{AFM}}$ is a BCS s-type and triplet p-type at $T > T_{\mathrm{AFM}}$. 2. What is the role of itinerant and localized electrons in creation of conditions for appearing of magnetism and superconductivity? 3. Which parts of crystal structure are responsible for magnetism and superconductivity? 4. What is the charge-type of conductivity: electrons or holes? We are going to give the answers in the next investigations.

3. Conclusion

For the first time:

1. We give the evidence that compound $\mathrm{Dy_{1-x}Y_xRh_4B_4}$ belongs to the family of metallic ferrimagnetic materials with so-called weak sublattice and has many interesting phase transitions when temperature decreases: paramagnetic – ferrimagnetic (collinear and not collinear) – spin-glass state – ferrimagnetic superconductor – antiferromagnetic superconductor.
2. We demonstrate that $\mathrm{DyRh_4B_4}$ has two Curie points.
3. We have measured the unusual dependences of the superconducting order parameter of $\mathrm{Dy_{0.8}Y_{0.2}Rh_4B_4}$ on temperature and magnetic field by using the Andreev-reflection point contact spectroscopy.
4. The obtained results give the background to say that compound $\mathrm{Dy_{1-x}Y_xRh_4B_4}$ is a candidate for spin–triplet symmetry of superconducting pairing.

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