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Ferromagnetism and superconductivity down to 0 K in b.c.t. $ErRh_4B_4$

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Résumé. — Nous avons préparé des composés $ErRh_4B_4$ de la structure type $LuRu_4B_4$ (quadratique centré) en introduisant des impuretés de carbone. La supraconductivité existe entre 0 et 7,5 K. La présence simultanée du ferromagnétisme est démontrée par un saut dans la variation thermique du flux gelé obtenu après une excursion dans un champ magnétique supérieur à H_{c2} et par l'existence d'un cycle d'hystérésis rectangulaire de l'aimantation. Ces effets donnent de nouveaux moyens d'investigation pour découvrir d'autres supraconducteurs ferromagnétiques.

Abstract. — We have prepared $ErRh_4B_4$ compounds with the body centred tetragonal structure (b.c.t.) of $LuRu_4B_4$ type using carbon doping. The superconductivity exists from 7.5 K down to 0 K. The simultaneous presence of ferromagnetism is shown by a jump in the thermal variation of the frozen flux obtained after decreasing the magnetic field from above H_{c2} and by the rectangular shape of the magnetization hysteresis. These effects give some new investigative tools for finding new ferromagnetic superconductors.

In recent years, several ternary compounds such as $ErRh_4B_4$ [1], $HoMo_6S_8$ [2] and $Sn_{13}Er_3Rh_4$ [3] have been extensively studied in connection with the interplay between superconductivity and ferromagnetism. The superconductivity exists between the temperatures T_{c2} and T_{c1} ($T_{c2} < T_{c1}$). Below T_{c2}, the compounds are ferromagnetically ordered. Nevertheless, neutron diffraction techniques have revealed [4, 5] that both the superconductivity and the ferromagnetic order coexist in a narrow range of temperature just above T_{c2}. A long wavelength oscillatory magnetization results from this competition in $ErRh_4B_4$ and $HoMo_6S_8$. A detailed study by neutron-diffraction on single crystals of $ErRh_4B_4$ [4] have also revealed the simultaneous presence of microscopic superconducting and ferromagnetic regions. The authors [4] suggest that the observation of ferromagnetic regions may be due to the existence of a vortex lattice in a ferromagnetic superconductor. The flux-free superconducting regions would contain the modulated magnetic structure within periodical distributions of ferromagnetic fluxoids. Such an interpretation needs to be verified by other experiments.

Our purpose, in the present study, is to find a situation in which the critical field H_{c2} is larger than $4\pi M_s$ [6], M_s being the spontaneous magnetization. In that case, we hope to extend the temperature range of coexistence of ferromagnetism and superconductivity down to 0 K. In type II superconductors, it is possible to increase H_{c2} by doping the compound with non-magnetic impurities. It is the reason why we have prepared $ErRh_4B_{4-x}C_x$ with $x = 0.2$. In fact, those impurities have stabilized the body centred tetragonal (b.c.t.) phase of $ErRh_4B_4$. This phase was previously discovered by Johnston [7] by alloying rhodium boride compounds with ruthenium. Up to now, this phase was considered as an antiferromagnetic phase [8]. Recently, Iwasaki *et al.* [9] have synthesized such a phase by creating a deficit in B atoms and have shown it to be superconducting down to 0 K with critical fields H_{c2} larger than 10 kOe. They claimed that Er atoms are antiferromagnetically ordered in that b.c.t. structure.

Using our doped compound $ErRh_4B_{4-x}C_x$, we found the same superconducting behaviour and, in contradiction with the previous results, a clear evidence in favour of the coexistence of ferromagnetism and superconductivity down to 0 K. The presence of ferromagnetism in the superconducting phase can be detected by a careful study of the magnetization hysteresis and of the frozen flux (due to pinning of vortices) which has to increase when a spontaneous magnetization appears below the Curie temperature.

1. Sample preparation and analysis.

The typical magnetic superconducting ternary boride $ErRh_4B_4$ for the case of stoichiometric composition is isostructural with the tetragonal compound $CeCo_4B_4$. Samples have been synthetized by arc-melting under purified argon from a mixture containing $ErB_4 + 4\,Rh + 0.2\,C$. X-ray diffraction data and microprobe analysis have shown that the samples obtained were not single phased. The compound $ErRh_3B_2$ (10-15 % in weight) and RhB have been detected as minor phases, the major phase being a ternary boride having the body-centred tetragonal $LuRu_4B_4$-type structure. In addition, the X-ray analysis does not reveal the presence of the tetragonal $ErRh_4B_4$ phase. It is quite likely that the rôle of the carbon atoms in the synthesis indicated above is to create boron vacancies in $ErRh_4B_4$. The $LuRu_4B_4$-type structure has already been found in arc-melted ingots slightly deficient in boron with respect to the composition $ErRh_4B_4$.

The difference between the crystal structures of $ErRh_4B_4$ and $ErRh_4B_{4-x}\square_x$ results only from the different arrangement of the Rh_4 tetrahedra. In $ErRh_4B_{4-x}\square_x$ ($LuRu_4B_4$-type) the tetrahedra in a same plane have different orientation but are distributed in an ordered way. In contrast, for $ErRh_4B_4$, the Rh_4 tetrahedra forming sheets perpendicular to the *c*-axis have the same orientation. The atomic arrangement of Er atoms is the same in both type-structures.

2. Susceptibility measurements.

We have measured the real (χ') and imaginary (χ'') components of the a.c. susceptibility between 7 and 35 K at a frequency of 21 Hz (Fig. 1). This susceptibility varies as a Curie law with a Curie constant corresponding to the free Er^{3+} ion value. A very weak peak of χ'' appears at about 25 K which is the ordering temperature of $ErRh_3B_2$ (not shown because invisible at the scale of the drawing). An enlarged view of the left-hand side of the diagram is shown on figure 2. This sample does not show the characteristic jump in χ' related to the superconductive transition ($T_c = 8.3$ K) of the tetragonal $ErRh_4B_4$ phase.

The transition temperature from the normal to the superconducting state is 7.6 K in agreement

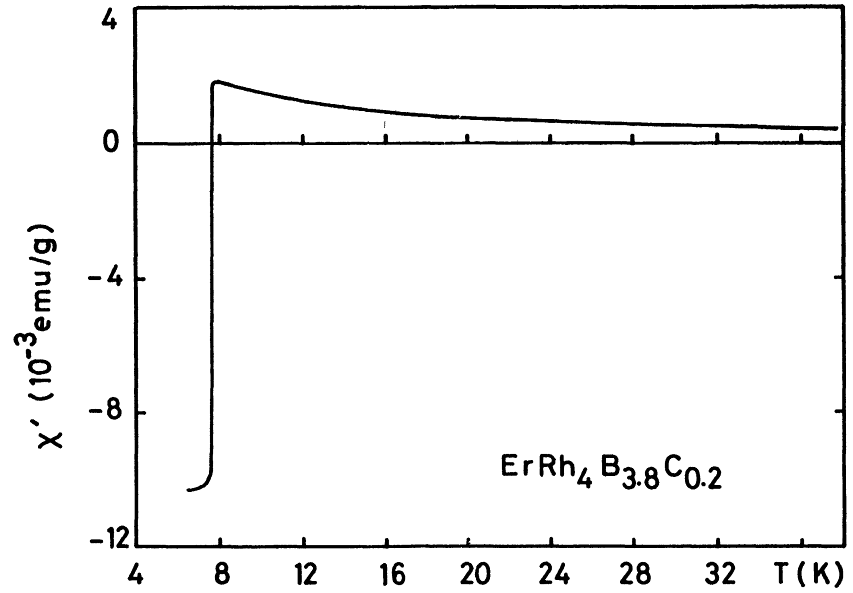

Fig. 1. — Real part of the a.c. susceptibility of ErRh$_4$B$_{3.8}$C$_{0.2}$ between 7 and 35 K.

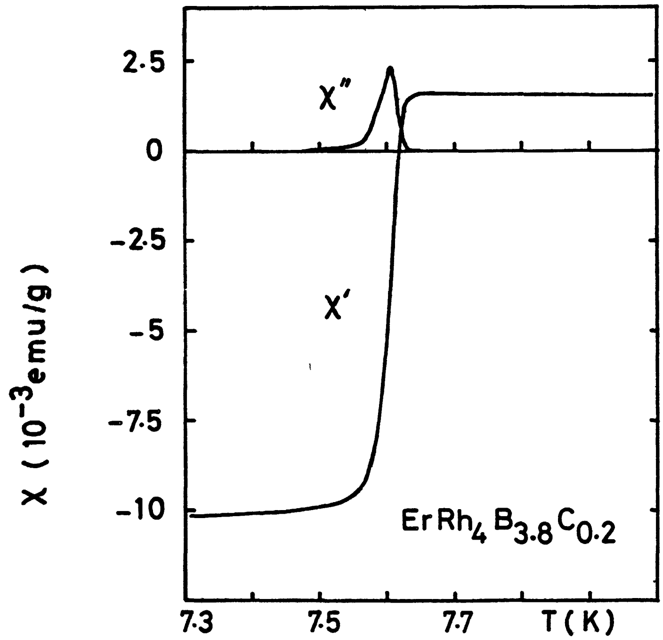

Fig. 2. — Superconducting transition of ErRh$_4$B$_{3.8}$C$_{0.2}$ measured with a mutual-inductance bridge (χ' real component, χ'' imaginary component), $f = 21$ Hz.

with previous results [9]. The change in susceptibility is equal to $-\frac{I}{4\pi(1-n)}$, n being the demagnetizing factor of our sample. We deduce $n = 0.23$ for the orientation of the sample with respect to the field. The transition width is very small and of the order of 0.1 K.

3. Low field magnetization.

We have measured the d.c. magnetization *versus* temperature in magnetic fields of 10, 20 and 50 Oe. The procedure was as follows : the sample was first heated up to 30 K and cooled down to 4.2 K in a zero field. The field was then applied and the measurements were done on warming up to 30 K followed by cooling down to 4.2 K in a constant field. The results are presented in figure 3. A striking feature is the lack of Meissner effect at the superconducting transition temperature on cooling in every field. We are unable to estimate the small change in the susceptibility dM/dH at the transition because we are observing a transition from the normal state, to a superconductive mixed state with strong pinning effects. As $(dM/dH)_H = 1/4\pi\beta(2\kappa_2^2 - 1)$, the Ginzburg-Landau parameter $\kappa_2^{(T=T_c)}$ [10] must be very large in this compound. We measured κ_2 equal to 30 on other samples. We deduced $dM/dH \simeq 4 \times 10^{-6}$ emu/g, and a quantity of this order is too small to be detected at the transition.

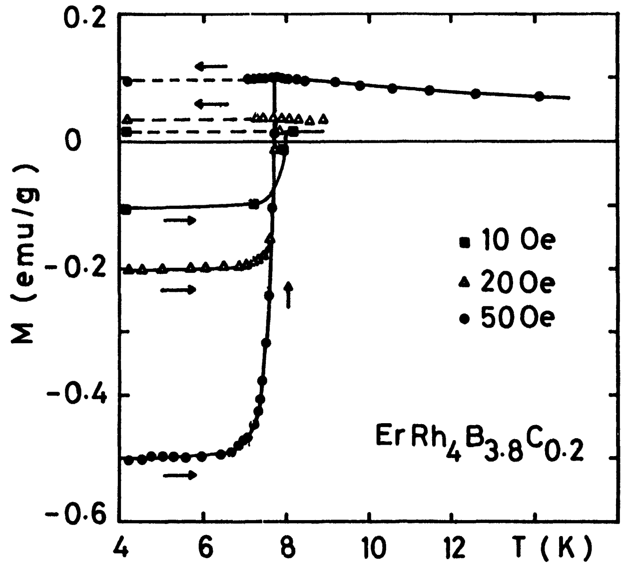

Fig. 3. — d.c. magnetization of $ErRh_4B_{3.8}C_{0.2}$ after cooling from 30 K in a zero field and applying fields of 10, 20, 50 Oe at 4.2 K. The temperature was first increased above T_c then decreased to 4.2 K in each field.

4. Upper critical field H_{c2}.

Resistivity and susceptibility measurements down to 20 mK show that our sample is still superconducting at this temperature. The critical field H_{c2} was estimated by extrapolation of the resistivity *versus* magnetic field curve to zero resistance (Fig. 4). Our phase diagram is similar to that proposed by Iwasaki *et al.* [9] (Fig. 5). The upper critical field H_{c2} of our sample is nearly three times larger than the critical field of the primitive $ErRh_4B_4$ [1]. The curve $H_{c2}(T)$ has a maximum around 3 K corresponding to a value of $H_{c2} = 16$ kOe ; the zero temperature value is 9 kOe. The broad transition in magnetic field indicates that some anisotropy of the critical field produces the progressive transition from the superconducting to the normal state in this polycrystalline sample [11]. No hysteresis has been observed on the resistivity when increasing or decreasing the applied magnetic field.

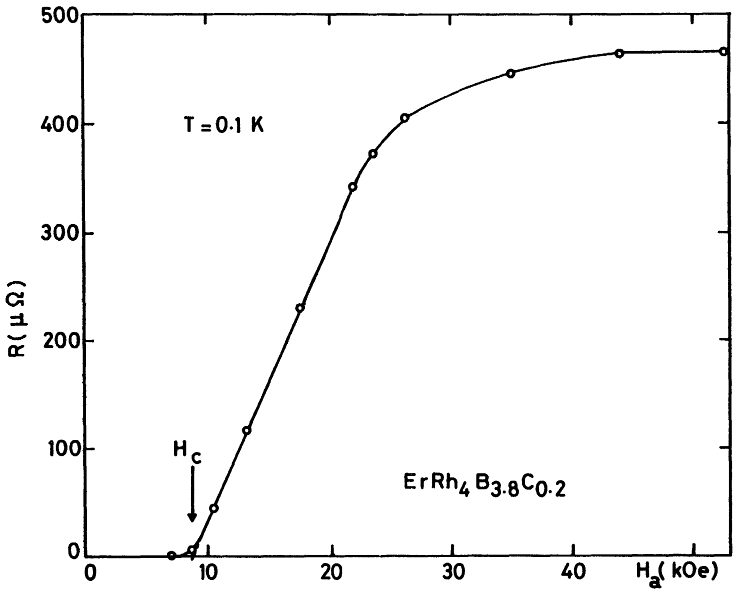

Fig. 4. — Typical curve of resistance *versus* applied magnetic field in $ErRh_4B_{3.8}C_{0.2}$. The current is parallel to the magnetic field.

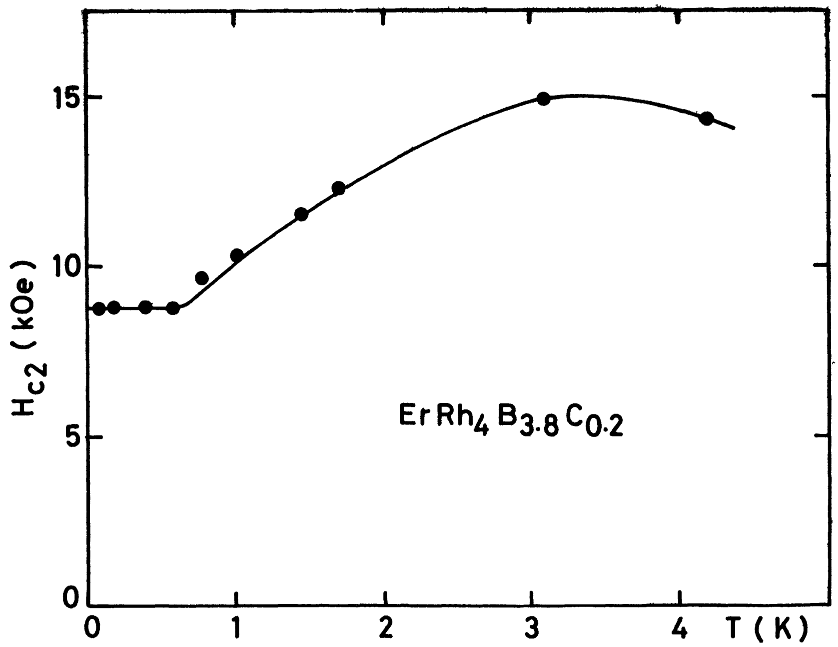

Fig. 5. — Upper critical field H_{c2} of $ErRh_4B_{3.8}C_{0.2}$ measured resistively as shown in figure 4.

5. High field magnetization and ferromagnetic hysteresis.

We have measured the hysteresis cycle for the magnetization M in applied fields up to 55 kOe larger than H_{c2}. In figure 6 a typical curve of M *versus* the applied field is shown together with

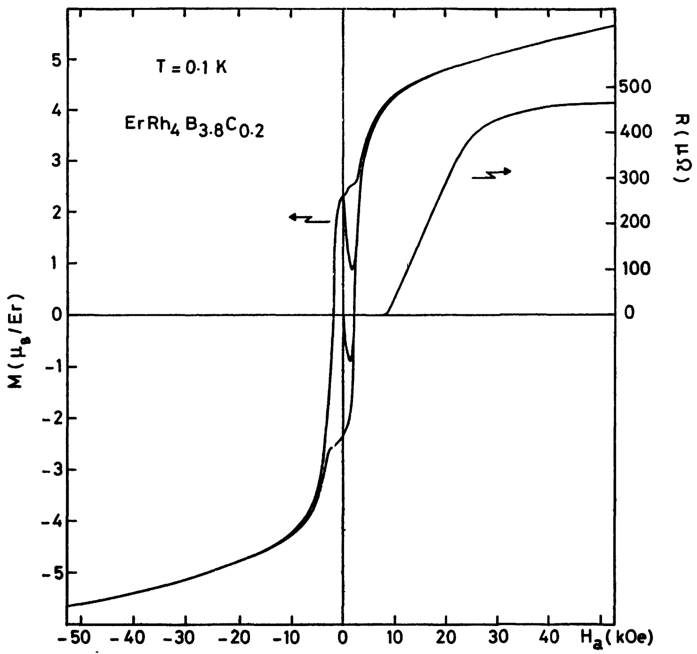

Fig. 6. — Magnetization (left scale) and resistance (right scale) of $ErRh_4B_{3.8}C_{0.2}$ at 0.1 K. *versus* applied magnetic field H_a measured in the same run. The current is parallel to the applied magnetic field.

the curve of R *versus* H measured in the same run. There is still no detectable change of (dM/dH) at $H = H_{c2}$ due to the very high value of the Ginzburg-Landau parameter [10]. On the same figure, are also shown the different magnetization curves obtained for different paths followed by the magnetic field. After decreasing the applied field H_a to $H_a = 0$, a negative slope, is obtained when again increasing the field in the positive direction (see Fig. 7). This effect clearly demonstrates the simultaneous presence of superconductivity in the sample. Such an effect has already been observed inside the hysteresis cycle of $Ce_{1-x}Gd_xRu_2$ [12].

In figure 7, we have plotted the magnetization M *versus* the internal field H_i. H_i is related to H_a by $H_i = H_a - 4\pi nM$. In this expression, n, the demagnetizing factor has been evaluated by setting the initial slope of the first magnetization $M(H)$ curve in the diamagnetic region equal to $-1/4\pi(1-n)$ when M is proportional to H ($H < 50$ Oe). The value obtained was 0.29 for the orientation of the sample with respect to the field. A nearly rectangular cycle is observed at $T = 150$ mK and 400 mK. The slope (dM/dH), of the « coercive field », is infinite as in some cases of hard ferromagnets. The magnetization hysteresis at 4.2 K is not rectangular even if the slope (dM/dH), for the value at the « coercive field » is 2 times larger than the susceptibility expected from a Curie law.

6. The jump of the frozen flux.

The frozen flux is the magnetization measured in a zero field after applying a 55 kOe field at constant temperature. As a function of temperature, an abrupt change of about 0.9 μ_B is observed at 700 mK (Fig. 8). This jump cannot be attributed to the ferromagnetic ordering of a parasitic phase $ErRh_4B_4$ which is not present in our sample. The disappearence of a spontaneous magnetization is the cause of this jump. The temperature at which the jump is observed could be the Curie temperature for the ferromagnetism of all the sample or it could correspond to the ferro-

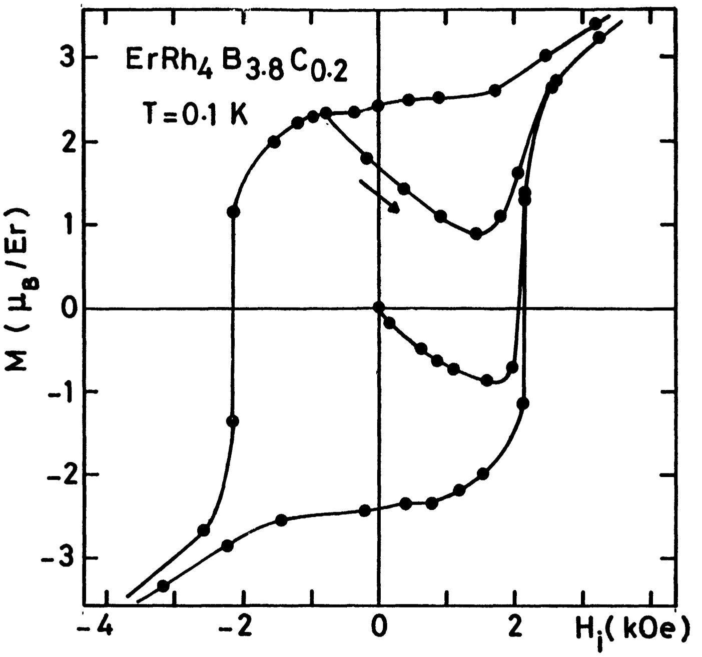

Fig. 7. — Magnetization hysteresis cycle at 0.1 K of $ErRh_4B_{3.8}C_{0.2}$ *versus* the internal field H_i.

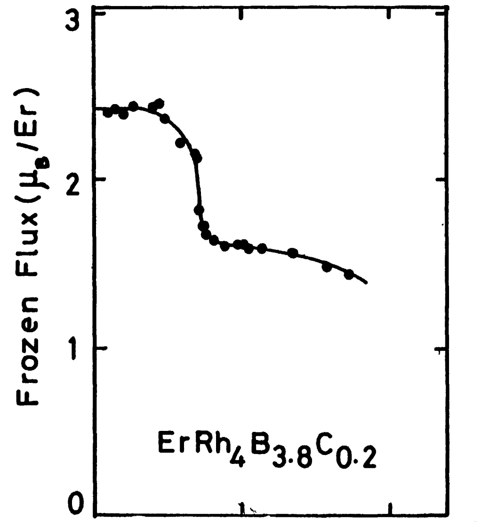

Fig. 8. — Variation of the frozen flux with temperature in $ErRh_4B_{3.8}C_{0.2}$.

magnetic ordering of the major part of the Er spins, whether or not we consider the possible existence of a small fraction of ferromagnetic inhomogeneities due to the $ErRh_3B_2$ into our sample [16].

7. Conclusions.

We have shown the coexistence of ferromagnetism and superconductivity down to a very low temperature into a body centred tetragonal phase of $ErRh_4B_4$. The critical temperature for the onset of superconductivity is 7.5 K. The Curie temperature of the major part of the Er spins seems to be 0.7 K. The ferromagnetic ordering of the Er spins does not destroy the superconductivity.

The observation of a rectangular hysteresis cycle of the magnetization inside the interval $(+ H_{c2}, - H_{c2})$ shows the spectacular phenomenon of reversing the ferromagnetic fluxoïds at a « coercive field ». It is one of the best tools of investigation to characterize new ferromagnetic superconductors. The thermal variation of the frozen flux (saturated remanent magnetization) is a window open inside the superconducting state which enables us to observe the appearance of a spontaneous magnetization below the Curie point.

By studying this doped compound, we have also shown that i) the upper critical field H_{c2} is larger than $4 \pi M_s \simeq 6.5$ kOe, ii) the Ginzburg-Landau parameter κ_2 of this superconductor is very high. Theoreticians [13-15] have shown that, under these circumstances, self-induced vortices spontaneously exist in a ferromagnetic superconductor. This compound could be a good example for such a phenomenon.

Acknowledgments.

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