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Superconductivity of domain walls in the ferromagnet HoMo₆S₈

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Résumé. — Nous avons étudié plusieurs échantillons de poudre recuite de Ho₁.₂Mo₆S₈ pur ou dopé. Nous avons observé une courbe de première aimantation à l'extérieur du cycle d'hystérésis, parfois une susceptibilité alternative diamagnétique dans l'état ferromagnétique, une grande magnétorésistance positive qui n'est pas d'origine magnétique, un cycle d'hystérésis de cette magnétorésistance, une variation de la résistance avec le courant et un trainage simultané de l'aimantation et de la résistance. Nous pensons que ces phénomènes peuvent être dus à la supraconductivité de parois de domaines qui exerce une influence sur la résistivité et le processus d'aimantation.

Abstract. — We have performed various measurements on annealed powder samples derived from Ho₁.₂Mo₆S₈. We have observed a first magnetization curve outside the hysteresis cycle, sometimes a diamagnetic a.c. susceptibility in the ferromagnetic state, a large positive magnetoresistance which is not of magnetic origin, an hysteresis cycle of the magnetoresistance, a variation of the resistance with the current, simultaneous after-effects on the magnetization and on the resistance. We believe that these results can be related to some superconductivity inside domain walls and to the influence of that state on the resistivity and on the process of magnetization.

1. Introduction.

The possible existence of superconductivity in ferromagnetic compounds has been discussed in the past. Ginzburg [1] pointed out the almost complete impossibility in practice, under ordinary conditions, to observe superconductivity in any kind of ferromagnets. This impossibility is due to the presence of a large spontaneous magnetization \( M_s \); the only possible case would be the one where \( 4 \pi M_s \) is smaller than the critical field \( H_c \). However, even if \( 4 \pi M_s > H_c \), the appearance of superconductivity, if otherwise possible, would be facilitated by geometric effects, negative field effects or domain configurations, which all tend to reduce the magnetic induction inside the sample. The boundaries of domains could be the regions where superconductivity could appear. Such an assumption has been made formerly by Matthias and Suhl [2] to explain the coexistence of superconductivity and ferromagnetism in Ce₁₋ₓGdₓRu₂ intermetallic compounds.

More recently, the calculations of Tachiki et al. [3] show that, in the ferromagnetic state of reentrant superconductors, the region inside the Bloch walls can become superconducting under some conditions. The arrangement of the spins inside the Bloch wall is indeed similar to a spin-spiral order. They suggested that this phenomenon could explain the lower value of the resistivity in the ferromagnetic state \( (T < T_{c2}) \) with respect to that in the normal state \( (T > T_{c1}) \). Superconducting regions remain in the sample and prevent the resistance from returning to its normal value except in fields high enough to erase the superconducting regions. For example, Fertig et al. [4] made resistance measurements on ErRh₄B₁₄ and found the resistance below \( T_{c2} \) to be about 40 % of the value above \( T_{c1} \); Ishikawa et al. [5], for their part, observed on Ho₁.₁₅Lu₀.₅Mo₆S₈ a linear decrease in the resistance with the temperature for \( T < T_{c1} \). The lowest value in that case was about 20 % of the normal state value. In both cases, a large positive magnetoresistance was observed in relatively moderate fields.
Our purpose in this paper is to corroborate the above assumption with new measurements and to focus our attention on some special properties which could be characteristic of superconducting Bloch walls.

2. Experimental details.

2.1 SAMPLES PREPARATION AND ANALYSIS. — The Ho\textsubscript{1.2}Mo\textsubscript{6}S\textsubscript{8} and Ho\textsubscript{1.2}Mo\textsubscript{5.8}Nb\textsubscript{0.2}S\textsubscript{8} samples were prepared by mixing, the starting materials in appropriate amounts. There were binary sulfide Ho\textsubscript{2}S\textsubscript{3}, molybdenum and niobium powder all reduced beforehand under hydrogen flow before adding sulfur crystals. The δ-Ho\textsubscript{2}S\textsubscript{3} binary was obtained by reduction of holmium oxide under a H\textsubscript{2}S flow at 1300 °C for four hours in a graphite crucible.

The mixed powder was pressed, and heated at 900 °C for 14 hours in an evacuated and sealed quartz tube. The reaction products were ground and mixed again, and a second heating was performed at 1100-1200 °C for 12 hours. A new annealing treatment was carried out to obtain pellets for physical study (6 h-1 250 °C). The other samples were prepared with turnings of holmium and molybdenum and grains of selenium. They were then introduced in a molybdenum crucible inside a silica tube. Heat treatment was then performed under the same conditions. The X-ray analysis shows the good phase with some impurities (~1-2 % Mo\textsubscript{2}S\textsubscript{3}, Mo or Ho\textsubscript{2}O\textsubscript{3}).

In the following experimental work, which attempts to demonstrate the presence of superconductivity inside domain walls, we can exclude the influence of a connected filamentary structure formed by a superconductive parasitic phase. In these chalcogenides, all the parasitic phases are known to be normal.

2.2 EXPERIMENTS. — To obtain a good thermal contact, the sintered samples were immersed in the mixing chamber of a 3He-4He dilution refrigerator. Fourprobe a.c. electrical resistance measurements were made in conjunction with magnetization measurements. The magnetic field ranged from 0 to 60 kOe and was applied perpendicularly to the direction of the current. Low frequency a.c. magnetic susceptibility measurements were made in the upper part of the mixing chamber prior to any application of large steady magnetic fields.

3. Results and discussion.

3.1 THE MAGNETORESISTANCE AND ITS HYSTERESIS CYCLE. — The resistance of Ho\textsubscript{1.2}Mo\textsubscript{6}S\textsubscript{8} and of Ho\textsubscript{1.2}Mo\textsubscript{5.8}Nb\textsubscript{0.2}S\textsubscript{8} are plotted against the external field in figure 1 at T = 2.5 K and T = 4.2 K respectively. In the normal paramagnetic region (T > T\textsubscript{c}), the change in resistance is too small to be evaluated when we increase the field from 0 to 50 kOe. At the same time, the paramagnetic Ho spins are gradually aligned in the direction of the field as shown by the magnetization curves plotted on the same figure. This clearly shows that the value of the resistance in the normal state, for these sintered samples, is too high to be modified by a negligible spin-disorder contribution.

The same measurements were made in the ferromagnetic region (T < T\textsubscript{c}) at 20 and 300 mK (Figs. 2 and 3) on Ho\textsubscript{1.2}Mo\textsubscript{6}S\textsubscript{8}. The resistance value in zero field is 10 % lower than the normal-state value. As shown above, this cannot be attributed to a spin-disorder contribution but rather to some superconductive paths in the sample. When we apply a field the resistance increases and reaches the normal-state value in a field of about 9 kOe. In that field, the magnetization is nearly saturated. The resistance shows an hysteresis cycle which follows the magnetization hysteresis cycle. The broader the magnetization cycle at different temperatures is, the broader the magnetoresistance cycle. The magnetoresistance is clearly related to the process of magnetization i.e. to the increase of the magnetization with field and then to the wall motion. When the magnetization becomes large, the length of the superconductive path decreases because we have less domain walls.

A detailed hysteresis cycle of the resistance for Ho\textsubscript{1.2}Mo\textsubscript{5.8}Nb\textsubscript{0.2}S\textsubscript{8} is shown in figure 4. The positive magnetoresistance reaches 25 % of the normal state.
value. This value is larger in this sample than it is in the non-doped one. The resistance increase in two steps could be due to two processes of magnetization: first the domain walls parallel (or perpendicular) to the field and then, in higher fields, the domain walls perpendicular (or parallel) to the field.

3.2 THE MAGNETORESISTANCE AND THE A.C. SUSCEPTIBILITY versus FIELD. — Figure 5 shows the a.c. susceptibility $\chi$ of Ho$_{1.2}$Mo$_{5.8}$Nb$_{0.2}$S$_8$ in different fields at $T = 400$ mK together with the magnetoresistance $\Delta \rho = (\rho_\infty - \rho_H)$ and the magnetization $M_0$. In a ferromagnet, $\chi_{a.e.}$ is proportional to the area of the domain walls [6] which have a reversible displacement at the frequency of measurements. Up to a field of 1 kOe, $\chi_{a.e.}$ is nearly constant. Thus we only have motion of domain walls without any change in their number. From 1 to 6 kOe, $\chi_{a.e.}$ decreases by a factor of 79% and reaches a plateau which seems to correspond to a new stable value of the area of the domain walls. At the same time $M$ increases, and the domain walls parallel to the field (or perpendicular) are expelled. From 6 to 11 kOe, a similar process

Fig. 2. — Magnetization and resistance of Ho$_{1.2}$Mo$_{5}S_8$ versus applied field at $T = 20$ mK.

Fig. 3. — Magnetization and resistance of Ho$_{1.2}$Mo$_{5}S_8$ versus applied field at $T = 300$ mK.

Fig. 4. — 4a : Hysteresis cycle of the resistance for Ho$_{1.2}$Mo$_{5}S_8$Nb$_{0.2}$S$_8$ in the ferromagnetic region. The resistivity in the normal state is equal to 1500 $\mu$ohm cm. 4b : Variation of the resistance with time for Ho$_{1.2}$Mo$_{5}S_8$Nb$_{0.2}$S$_8$.

Fig. 5. — Magnetization $M$, a.c. susceptibility $\chi_{a.e.}$ and magnetoresistance $\Delta R$ of Ho$_{1.2}$Mo$_{5}S_8$Nb$_{0.2}$S$_8$ at $T = 0.4$ K versus applied field.
occurs, this time for the walls nearly perpendicular (or parallel) to the field.

The variation of $\Delta p$ with the field is similar to the one of $X_{ac}$ except for very low fields. As the area of the domain walls decreases, so does the length of superconductive paths and accordingly $\Delta p$. In a field of about 11 kOe, the domain walls are expelled and the resistance reaches the normal state value.

In very low fields, the resistance seems to increase faster than $X_{ac}$ does. There must be another contribution to the magnetoresistance depending more on $M$ than on the motion of the domains walls. This can be due to the tunnel effect of superconductive pairs between close domain walls belonging to different grains and separated by normal ferromagnetic regions (see section 3.5). The superconductivity induced through these junctions could be easily destroyed under the application of small fields.

### 3.3 Simultaneous time effects on the magnetization and on the resistivity.

While measuring the resistance of $\text{Ho}_{1.2}\text{Mo}_{5.8}\text{Nb}_{0.2}\text{S}_8$ (Fig. 4), the magnetization was only measured in zero field after applying a 60 kOe field. The remanent magnetization was initially equal to 19 000 u.c.m./mole ($3.4 \mu_B$/Ho). A large time dependence is observed both in resistivity and in magnetization (Fig. 4, lower part). After 2 hours, the remanent magnetization has been divided by a factor of 2 while the resistivity decreases as shown. This fact is another proof which confirms our supposition of superconducting domain walls. The time effect on the resistivity in zero field is a strong indication that the motion of the domain walls in each grain has not only reduced the remanent magnetization but also increased the superconductive percolation between the walls of different grains.

We made more careful measurements on the same sample at $T = 0.15$ K. Starting from a demagnetized state, both $M$ and $R$ were measured in a constant field of 900 Oe (Fig. 6) as a function of time. $R$ and $M$ have a similar variation, both increasing with time. Plotting $R$ versus $M$ (Fig. 7), we observe nearly a straight line. It is thus obvious that the time effects on $R$ are governed by the time dependence of $M$.

### 3.4 Critical field and magnetoresistance.

We have measured the critical field of $\text{Ho}_{1.2}\text{Mo}_5\text{S}_8$ and $\text{Ho}_{1.2}\text{Mo}_{5.8}\text{Nb}_{0.2}\text{S}_8$ (Fig. 8). The critical field, in this case, is defined by the extrapolation to $R = 0$ of the linear part of the curve $R(H)$. It is then lower than the usual values determined by $R = R_{sat}/2$. The maximum value is about 2 times larger in the doped sample than in the pure one. We can bring together the enhancement of the critical field and the enhancement of the magnetoresistance.

To obtain the saturated value of the resistance, a larger field (11 kOe) is needed in the case of the doped sample than in the case of the pure one (9 kOe). Two reasons for this can be put forward. First, the mobility of the domain walls is lower for the doped sample because the added impurities play a rôle of pinning...
centres. So, the domain walls disappear in a higher field. Secondly, the critical field of the domain walls has been increased by doping. In every way, the critical field of the domain walls is much larger than the B.C.S. value we can deduce from the curve $H_c(T)$ near $T_c$ by

$$H_c(0) = 0.69 \ T_c \left( \frac{dH_c}{dT} \right)_{T_c}$$

(in our case $H_c(0) = 2.6$ kOe) and also larger than any critical field measured resistively in the paramagnetic region just above the Curie temperature.

Below the Curie temperature, the resistance is not zero even if the domain walls structure is present throughout the sample. In this kind of sample, there is no percolation of a superconductive path from one end to the other. This is due to the sintered nature of these compounds. The contacts between particles are very bad, indeed, the residual resistivity is 10 times larger than the residual resistivity of single crystals [7] or of sputtered samples [8]. It is impossible for the domain walls to be continuous from one particle to the other due to the presence of some insulating barrier and due to the anisotropy which orientates the walls. However tunelling effects may exist between particles. We present evidence for this effect in the following section.

### 3.5 JOSEPHSON EFFECT BETWEEN SUPERCONDUCTIVE PARTICLES.

#### 3.5.1 Susceptibility measurements.

A multiconnected network of Josephson weak links has been obtained by Ishida and Mazaki [9] by introducing technetium in the pores of alumina. They observed that the a.c. susceptibility near the superconductive transition is very sensitive to the amplitude of an a.c. field. The higher the a.c. field is, the broader the transition, but the onset temperature of the transition holds the same value. They also observed structures in the off-balance signal related to flux quantum entrance into superconducting loops.

Rosenblatt et al. [10] have shown that, in an assembly of bulk superconducting particles coupled through Josephson weak links, the transition appears in two steps i.e. at a single particle ordering temperature and at a long range ordering temperature.

We have measured the a.c. susceptibility $\chi_{a.c.}$ of several Chevrel phases for different amplitudes of the a.c. field $h_0$. The results for $\text{Ho}_{1.2}\text{Mo}_6\text{S}_8$ and $\text{Ho}_{1.2}\text{Mo}_{5.8}\text{Nb}_{0.2}\text{S}_8$ are shown on figure 9. As previously observed, the width of the superconducting transition depends on the amplitude of $h_0$. The deviation of $\chi_{a.c.}$ from the paramagnetic state occurs at the same temperature and full diamagnetism is observed at lower temperatures. We also made direct observation of the off-balance signal coming from the secondary circuit of the mutual inductance. The wave-form has many structures as previously observed in a multiconnected Josephson network. A more careful study is now in progress.

The properties of our samples are very similar to those observed in superconductive particles coupled by Josephson junctions. In our sintered samples, superconducting particles must be separated by oxide layers. Then, in the ferromagnetic region, it will be more difficult to observe the percolation from particle to particle of superconductive domain walls. However, such a percolation should be possible in single crystals depending on the existence of superconductivity not only in the 180° or 90° walls but also in the walls of closure domains.

#### 3.5.2 Influence of current intensity on resistivity.

We have measured, in the ferromagnetic state, the resistance of $\text{Ho}_{0.2}\text{Mo}_{5.8}\text{Nb}_{0.2}\text{S}_8$ with several current intensities (Fig. 10). In low fields (i.e. in the region where we observe a magnetoresistance) a small non-linear effect is observed. By increasing the current we increase the resistivity because the critical current of some Josephson junctions is attained. In high fields, the resistance is nearly constant because the domain walls are no longer superconducting.

### 3.6 OBSERVATION OF A NEGATIVE A.C. SUSCEPTIBILITY INTO THE FERROMAGNETIC STATE.

We have measured the a.c. susceptibility of $\text{HoMo}_6\text{S}_8$, of
HoMo5.9Nb0.1S8 and of HoMo5.9S7.9Se0.1 in a constant a.c. field (Fig. 11). We thought that these compounds would be reentrant superconductors. It is obviously not the case. A single transition is observed and marked by a sharp peak at 1 K. It could lead to a ferromagnetic or a superconductive transition. There is no sign, on the susceptibility, of reentrance in the ferromagnetic state if the phase transition at 1 K is superconductive in nature. The magnetization of HoMo5.9Nb0.1S8, measured at 20 mK, is plotted in figure 12. This curve is similar to the hysteresis cycle of a ferromagnet. In addition, the resistance of that sample (Fig. 13) is weakly decreasing with temperature without visible superconductive transition. These two facts, taken together, are strong arguments in favour of a ferromagnetic transition instead of a superconductive one. In spite of the presence of ferromagnetism, the susceptibility at 20 mK is diamagnetic and equal to 25% of (-1/4π).

These properties show that superconductivity can exist in each particle of the sintered sample inside the ferromagnetic state without percolation. This superconductivity seems to be developed in large areas because we have attained a large value for diamagnetic susceptibility. This result is largely in favour of the superconductivity of domain walls.

3.7 FIRST MAGNETIZATION CURVE OUTSIDE THE Hysteresis CYCLE. — A first magnetization curve outside the hysteresis cycle has been observed by Ishikawa [11]. No explanation was given for this behaviour. For our part, we have also observed such a behaviour in almost every sample we have measured (see for example Fig. 12). A possible explanation is as follows. Generally, when a magnetic field is applied to a ferromagnetic metal, eddy currents are generated.
and create a field acting in opposition to the applied field. In cases where superconductive closed surfaces should be present, this cancellation will be more efficient. The first magnetization curve must be very sensitive to such effects, up to the critical field of the superconductive area. This behaviour seems to be one of the most characteristic properties in order to recognize a superconductive area in a ferromagnetic sample.

4. Conclusion.

We have attempted to demonstrate the presence of superconductivity inside domain walls in the ferromagnetic state of some Chevrel phases.

The strong positive magnetoresistance in the ferromagnetic state and its hysteresis cycle, the variation of the resistivity with time, are results in favour of superconductivity inside the domain walls.

The existence of a large diamagnetic susceptibility in some cases, the presence of a screening effect which induces a first magnetization curve outside the hysteresis cycle and some non linearity in the resistance versus the current are also good arguments in favour of the presence of superconductivity in domain walls instead of fluctuations.

The same study has to be made on single crystals to confirm this point. We expect that single crystals showing reentrant superconductivity would be apparently superconductive because the domain walls occupy large continuous areas throughout the sample. The percolation of such superconductive paths would be possible in the ferromagnetic state of such crystals if the closure domains also have superconductive walls.

In order to interpret our results we need calculations which take into account the influence of the superconductivity on the irreversible and reversible motion of domain walls. From our experimental results, we feel that the ferromagnetic compounds become softer in the presence of such a superconductivity as we have observed a large time dependence of the magnetization far below the Curie temperature.

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