LONG RANGE MAGNETIC ORDER IN THE SUPERCONDUCTING STATE OF HEAVY RARE EARTH MOLYBDENUM SULFIDES AND THEIR PSEUDOTERNARY COMPOUNDS

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Résumé.- On présente les observations expérimentales prouvant l'existence d'un ordre magnétique à longue portée à l'état supraconducteur dans les sulfures ternaires de molybdène et de terres rares (TR variant de Gd à Er). Parmi ces observations figurent des résultats d'expériences de diffraction neutronique dans certains cas. Les propriétés magnétiques et supraconductrices de cette série de composés sont discutées et des résultats préliminaires concernant (Ho-Lu)Mo_6S_8 sont également exposés.

Abstract.- Various experimental evidences for long range magnetic order in the superconducting state of the heavy rare earth molybdenum sulfides (RE)Mo_6S_8 (RE = from Gd to Er) are presented together with the results of recent neutron diffraction studies on some of these sulfides. Their magnetic and superconducting properties along the rare earth series in the Periodic Table are discussed, and preliminary results on speudoternary compounds of Ho are also included.

Ever since Ginzburg studied /1/ the problem about twenty years ago, a great deal of effort has been made in the quest for the coexistence of superconductivity and magnetism /2/. Earlier experiments were, however, carried out exclusively on dilute substitutional alloy systems and in such systems the superconductivity was often suppressed well before the concentration of magnetic ions became sufficiently high for a long range magnetic order /3/. Nevertheless, some evidence of a long range magnetic order has been suggested in several ingeniously compounded alloys, but all of such magnetic orders turned out ot be of short range ; either spin glass - or cluster - type with a correlation length shorter than 50 Å /4/. Such a frustrating difficulty with dilute substitutional alloys has been overcome only after the recent discoveries /5/ of superconducting stoichiometric rare earth compounds, which contain as much as 7 to 10 at. % of magnetic rare earth (RE) ions distributed over regular lattice sites, about 6.5 Å apart. It is this property of such new compounds which provides us with a possible coexistence of superconductivity with a long range magnetic order. As a matter of fact, soon after these discoveries, a long range magnetic order was found almost at the same time in $Ho_{1.2}Mo_6S_8$ /6/ and $ErRh_4B_4$ /7/. The long range magnetic order appeared in their superconducting state, but it was accompanied by a destruction of superconductivity at its onset. Soon later, however , in some other RE molybdenum sulfides /8/ and selenides /9/, (RE)Mo_6X_8 (X = S or Se), so-called Chevrel compounds /10/, various evidences of coexistence with a long range magnetic order have been reported : in (RE)Mo_6S_8 (RE = Tb, Dy and Er) /8/, for example, resistance anomalies in their superconducting state were found and interpreted as a result of a long range magnetic order with the aid of ac susceptibility and magnetization measurements. The long range antiferromagnetic order was, in fact, confirmed for RE = Dy /11/ and Tb /12/ by recent neutron diffraction experiments performed at Brookhaven National Laboratory. Subsequently, a similar resistance anomaly was also found in $Gd_{1.2}Mo_6S_8$. Therefore, all these results on (RE)Mo_6S_8 allow us a systematic study of various magnetic and superconducting properties across the series of the heavy rare earth ions in the Periodic Table. As some details about (RE)Rh_4B_4 and (RE)Mo_6Se_8 will be reviewed by Dr. M.B. Maple elsewhere in this volume, experimental results regarding the coexistence problem only in the heavy rare earth molybdenum sulfides and their pseudoternary compounds are presented in this article.

First some of the previous results on (RE)Mo_6S_8 are here recapitulated, before more specifics of each compound are discussed : all of these compounds from Gd to Er become superconducting below about 2 K and show a magnetic phase transition at a lower temperature, coexisting with the superconductivity for RE = GD, Tb, Dy and Er, while for RE = Ho destroying the superconductivity at the onset of a ferromagnetic order. Accordingly it is extremely

interesting to see what happens if some Ho ions in $HoMo_6S_8$ are replaced by non-magnetic ions to slightly weaken the strong ferromagnetic interaction preventing the coexistence with the ferromagnetic interaction preventing the coexistence with the ferromagnetism in this compound. Some preliminary results on speudoternary compounds are also included in this article. Although the long range nature of these magnetic orders has been so far confirmed only for RE = Tb, Dy and Ho with neutron experiments, all magnetic orders are expected to be of long range judging from similarities in their orther properties such as magnetization and temperature dependence of upper critical fields. This long range nature in these compounds, indeed, makes one of the most important differences from the magnetic states found previously in dilute substitutional alloys.

The reentrant behavior of $Ho_{1.2}Mo_6S_8$ /6/ is shown in figure 1, where its ac susceptibilities, χ_{ac} are plotted as functions of temperature ; the compound becomes superconducting below about 1.2 K (This value for this particular sample is, however, much lower than more representative values, see figure 9), and returns to the normal state at 0.65 K where a long range ferromagnetic order establishes itself.

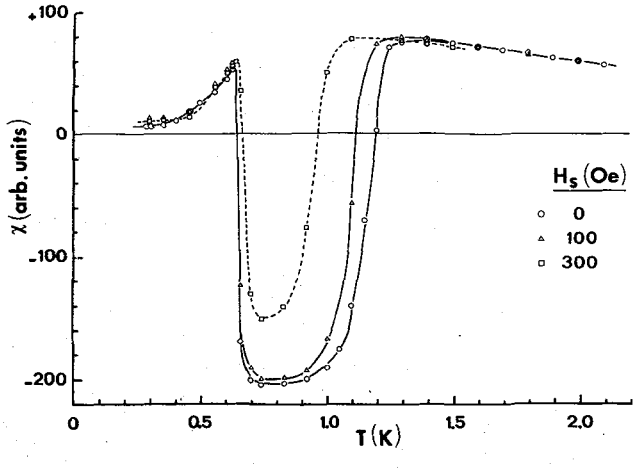

Fig. 1 : ac magnetic susceptibility of $Ho_{1.2}Mo_6S_8$ as a function of temperature, showing the reentrant behavior (ref. 6).

The long range ferromagnetism was later confirmed by a neutron experiment /13/ : the Ho ions in the Chevrel phase are aligned along the [111] ternary axis with a magnetic correlation length longer than 300 Å.

In the following, experimental evidences for a long range antiferromagnetic order in Er, Dy, Tb and Gd compounds are presented with an emphasis on the particularities of each compound. In figure 2, the resistance anomaly of $Er_{1.2}Mo_6S_8$ in the superconducting state is shown.

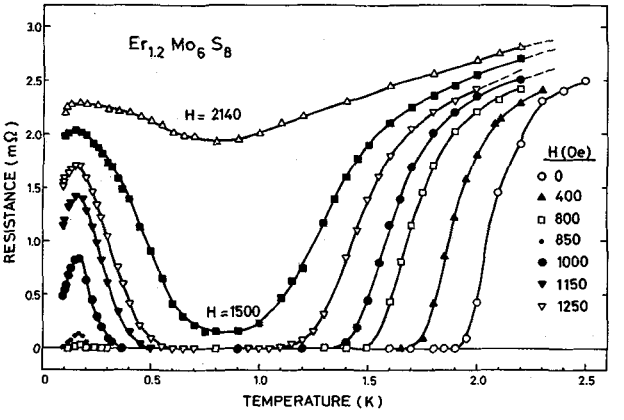

Fig. 2 : Resistance vs temperature for $Er_{1.2}Mo_6S_8$ in magnetic fields between 0 and 2.14 kOe (Ref. /8/).

This compound remains superconducting below 2.1 K down to the lowest temperature investigated in zero magnetic field, but the weakening of the superconducting screening effect by the application of magnetic fields higher than about 800 Oe reveals an anomaly which is peaked at 0.16 K, independent of the field. This anomaly disappears and the full superconductivity is restored at low enough temperatures. A very similar behavior in R vs T was found also in $Dy_{1.2}Mo_6S_8$ as shown in figure 3.

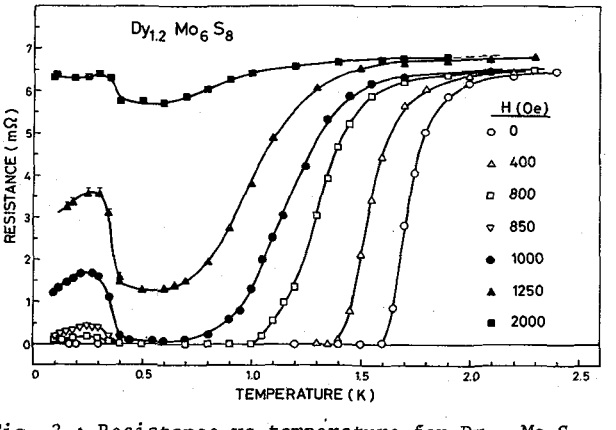

Fig. 3 : Resistance vs temperature for $Dy_{1.2}Mo_6S_8$ in magnetic fields between 0 and 2 kOe (Ref. /8/).

However, this compound shows a relatively abrupt rise of R at about 0.4 K which is reflected in its anomalous upper critical field curve as discussed below. In figure 4, the spectra obtained by a recent elastic neutron diffraction experiment /11/ are shown for the antiferromagnetic (upper spectrum) and the paramagnetic superconducting state (lower spec-

trum).

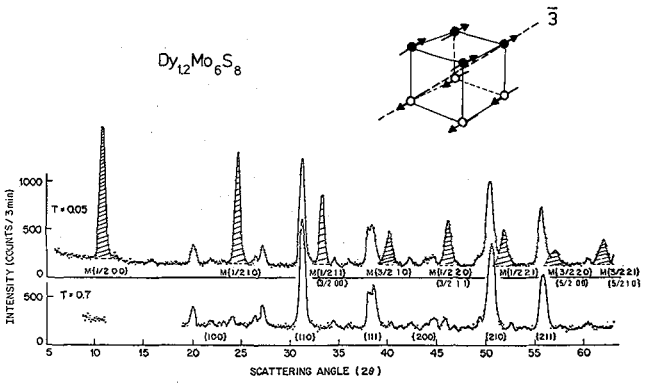

Fig. 4 : Powder neutron diffraction spectra (Ref. 11) for $Dy_{1.2}Mo_6S_8$ above (T = 0.7 K) and below (T = 0.05 K) its magnetic transition. The inset shows the antiferromagnetic arrangement of moments along the ternary axis, $\bar{3}$.

The eight magnetic peaks (cross-hatched) in the range of scattering angles (2θ) up to 63° were successfully indexed on the basis of the simple cubic Chevrel lattice (with a slight rhombohedral distortion) : the inset shows a half of the tetragonal magnetic unit cell with the moments on {100} planes alternately parallel and antiparallel to the $[11\bar{1}]$ ternary axis. These results conclusively confirm /11/ that the Dy ions in the main Chevrel phase, rather than in a second phase develop a long range antiferromagnetic order. The extra Dy ions of 0.2 per formula unit are probably the cause of a few extra small magnetic peaks in the spectra /11/. A similar long range antiferromagnetic order was confirmed also for $Tb_{1.2}Mo_6S_8$ by another neutron experiment /12/. This antiferromagnetic order below its magnetic ordering temperature of 1 K is demonstrated by the low values of magnetization for $H \lesssim 1.5$ kOe, in figure 5.

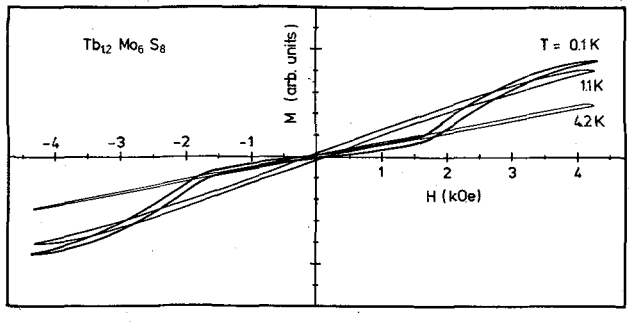

Fig. 5 : Magnetization vs applied magnetic field for $Tb_{1.2}Mo_6S_8$, showing an antiferromagnetic behavior at T = 0.1 K (Ref. /14/).

In higher fields, the magnetic moments flip over along the applied field direction. However, even at 18.5 kOe a complete saturation of the moments could not be attained. This unusually slow saturation process, which is not well understood at the moment, seems to be characteristic of these compounds /14/.

In figure 6, χ_{ac} of $Gd_{1.2}Mo_6S_8$ as a function of temperature is shown for H = 0 and 400 Oe. It should be remarked that such a pronounced peak of χ_{ac} in zero applied magnetic field was found only for this compound in this series. This anomaly in χ_{ac} may be explained as a result of a stronger exchange scattering effect in this compound than in the others which is reflected also in its large suppression of T_c and upper critical fields as shown in figures 8 and 9. Because an almost identical M-H curve to that shown in figure 5 was found /14/ for this compound, the magnetic state below 0.95 K appears to be also long range antiferromagnetic.

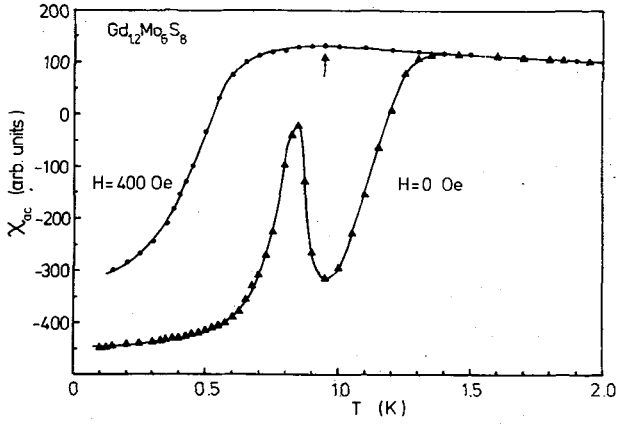

Fig. 6 : ac susceptibility vs temperature for $Gd_{1.2}Mo_6S_8$. The arrow indicates the ordering temperature where χ_{ac} deviates from the Curie-Weiss law.

From the resistance measurements in magnetic fields, upper critical fields are determined as reported earlier /8/. The results are summarized in figure 7 and 8 for RE = Ho and Dy, and Gd and Tb, respectively in order to show the apparent importance of specific magnetic interactions in characterizing these anomalous H_{c2} curves. The curves down to their magnetic ordering temperatures, T_m were successfully fitted as shown by the solid lines in the figure and interpreted as the spin polarization effect in the framework of the additive pair breaking theory as described elsewhere /8/. Below their T_m's, however, a sudden decrease of H_c is accompanied for these compounds ; this decrease at T_m is very abrupt in both Dy and Ho compounds and seems to be due to a rather strong ferromagnetic interaction in these com-

pounds. In fact, the magnetization measurements

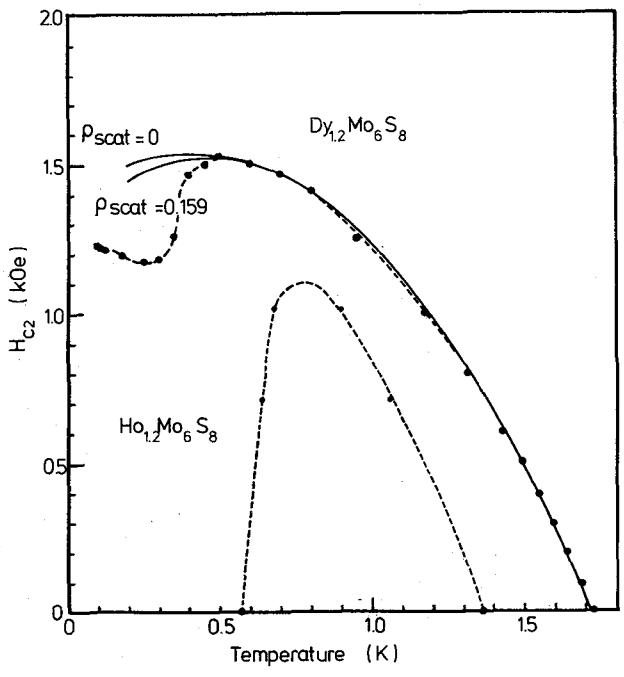

Fig. 7 : Superconducting upper critical field vs temperature for $Dy_{1.2}Mo_6S_8$ and $Ho_{1.2}Mo_6S_8$, showing an abrupt decrease at T_m.

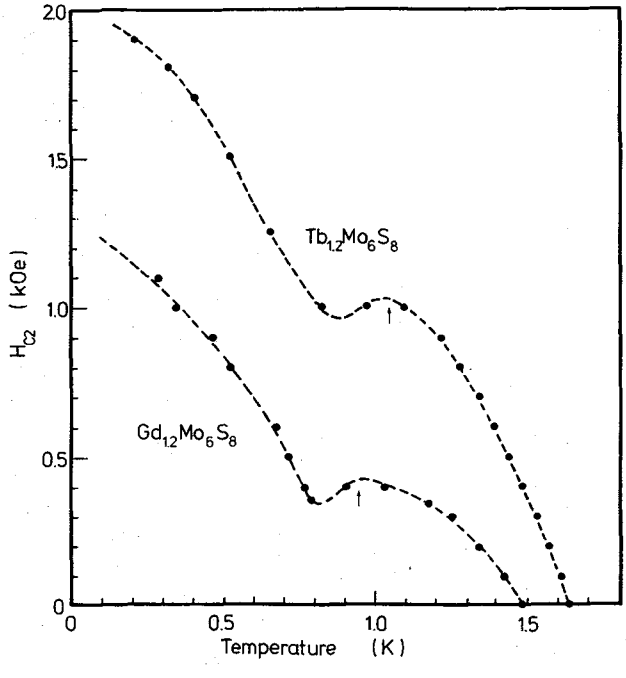

Fig. 8 : Upper critical field vs temperature for $Tb_{1.2}Mo_6S_8$ and $Gd_{1.2}Mo_6S_8$. The arrows shows their magnetic ordering temperatures.

showed /14/ that the magnetic moments in the Dy compound are also ferromagnetically aligned in fields higher than about 1.3 kOe. On the other hand, in the Tb and Gd compounds, there is a broad peak around T_m (indicated by an arrow), where the moments are still aligned antiferromagnetically in the corresponding fields /14/. The peak is followed by a sharp rise at lower temperatures, as shown in figure 8. This sharp rise is a result of the fast recovery of superconductivity in the well ordered antiferromagnetic state as evidenced in their χ_{ac} - and R-T curves. One notes that the variation of the H_{c_2} below T_m for the Dy compound is much smaller. This apparent difference may be, however, simply due to its much lower T_m compared with T_c for this compound.

In figure 9 are summarized the magnetic ordering temperature, T_m and the superconducting transition temperature, T_c, of all the compounds discussed above /15/ in order to show their general trend across the heavy rare earth series in the Periodic Table. Magnetic orderings in metallic subs-

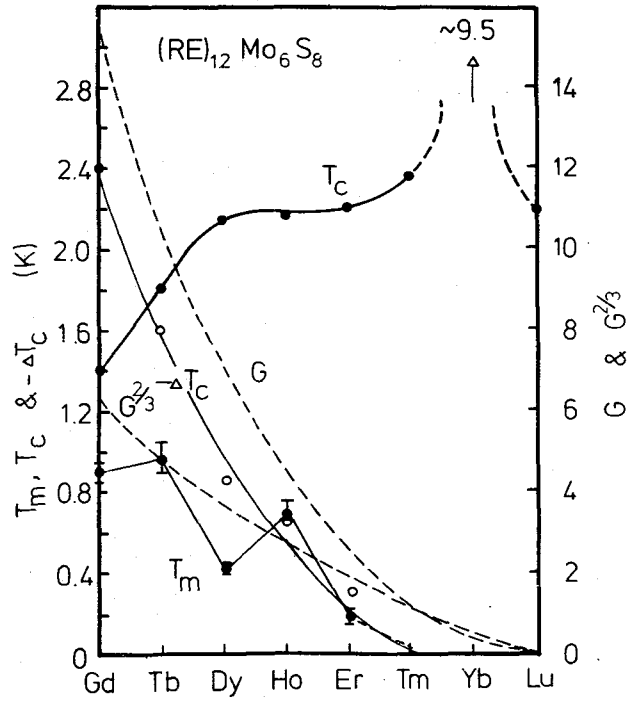

Fig. 9 : T_m, T_c, decrease of T_c, $-\Delta T_c$, de Gennes factor, G and $G^{2/3}$ for heavy rare earth molybdenum sulfides (Ref. /14/).

tances, in general, result from a complex combination of interactions of various origins /16/, such as an indirect exchange interaction mediated by conduction electrons and an anisotropic interaction caused by crystal fields to which magnetic ions in crystals are subjected. In addition to our still poor under-

standing of the detailed electronic and crystallographic properties of these complex ternary compounds, the small interaction energies involved in these magnetic transitions as evidenced by their low ordering temperatures make the discussion extremely difficult. Therefore, some possible mechanisms for the magnetic orderings in these compounds are briefly discussed and the details must be left for future studies.

If the RKKY type indirect exchange interaction /17/ is predominantly responsible as in pure heavy rare earth metals T_m would vary with the de Gennes factor, G, defined as $(g-1)^2 J(J+1)$. In fact, the molecular expression for T_m is given by /18/

$$k_B T_m = \frac{CN\chi_o}{12\mu_B^2} G\Gamma^2.$$

C is the concentration of magnetic ions, χ_o is the paramagnetic susceptibility of the conduction electrons and Γ is the exchange interaction constant defined by $H_{ex} = -\frac{1}{N}\sum_i (g-1)\Gamma \vec{J}_i.\vec{S}$, where N is the total number of atoms perunit volume, $\vec{J}$ is the total angular momentum of the RE ion and $\vec{S}$ is the electron spin. As can be seen in the figure, however, T_m for these compounds varies approximately with $G^{2/3}$ as found in many binary alloys of the rare earth metals /19/. Furthermore, as pointed out earlier /14/, the zigzag variation of T_m suggests that the interaction is modulated by an anisotropic interaction such as the crystalline field effect particular to each RE ion, possibly acting differently on the Kramers (Gd, Dy and Er) and the non Kramers ions (Tb and Ho). Other mechanisms such as a superexchange interaction via sulfur atoms between the RE ions and the classical magnetic dipolar interaction could be also responsible for these low temperature orderings.

It should be also pointed out that the direction of the magnetic moments in both ferro- and antiferromagnetic structures coincides with the unique crystallographic ternary axis of the Chevrel phase /11-13/. This might suggest the importance of the anisotropy caused by the sulfur atoms around each RE ion in determining the easy direction of the moments in these compounds. In fact, a cube formed by the eight sulfur atoms surrounding a RE ion is compressed along the ternary axis /20/.

In spite of these reservations concerning the magnetic orderings in these compounds, it seems worthwhile to estimate the order of magnitude of the exchange constant, using the above formula based on the RKKY interaction. The value of Γ can be alternatively estimated from the decrease of T_c, $-\Delta T_c$ due to spin exchange scattering /21/, using the following formula /22/

$$k_B \Delta T_c = \frac{\pi^2}{8} CN(0) G\Gamma^2$$

where N(0) is the electronic density of states per eV-atom-spin. For this calculation, the T_c's of hypothetical non magnetic compounds are required. However for these dense magnetic compounds, it is difficult to separate the spin exchange effect from other chemical effects. Hence, $La_{1-x}Lu_xMo_6S_8$ /23/ have been tentatively chosen as non magnetic compounds. Thus chosen $-\Delta T_c$'s vary approximately with G as expected from the formula (see figure 9). The values of Γ determined with the two methods for the Dy compound, for example, were 50 and 25 meV, respectively. It was found /14/ that either method yields a reasonably constant Γ across the heavy rare earth series, although the values determined from T_m where appreciably larger than those from $-\Delta T_c$. These values of Γ for the Chevrel compounds are considerably smaller than those of other RE compounds /24/, as expected from the fact that the RE ions in the Chevrel compounds are well separated (about 6.5 Å apart).

As stated in the beginning, for our understanding of the problem regarding a possible coexistence of ferromagnetism and superconductivity, it is very important to study slightly diluted Ho compounds with non magnetic ions. For this purpose, $Ho_{1.2-x}Lu_xMo_6S_8$ ($0 \leq x \leq 0.2$) have been chosen : the dilution with Lu resulted in a slight decrease of T_m, as expected, from 0.75 K for x = 0 to 0.65 K for x = 0.2, but without any appreciable change of T_c. This fact indicates that the spin effect is not sufficient to predict a change of T_c in these compounds. Therefore, at the moment it is difficult to make a comparison with theoretical predictions /25/. In figure 10, the dc resistance of $Ho_{1.15}Lu_{0.05}Mo_6S_8$ is shown as a function of temperature and applied magnetic field. Although this sample showed a very similar χ_{ac} -T curve to that of $Ho_{1.2}Mo_6S_8$, the linear decrease of R with temperature in zero magnetic field suggests that the sample would eventually become superconducting at very low temperatures. If the magnetic state is ferromagnetic as in $Ho_{1.2}Mo_6S_8$ this may be the first example of the coexistence

with ferromagnetism. In order to clarify these questions, more experiments are in progress together with some other pseudoternary compounds of Ho.

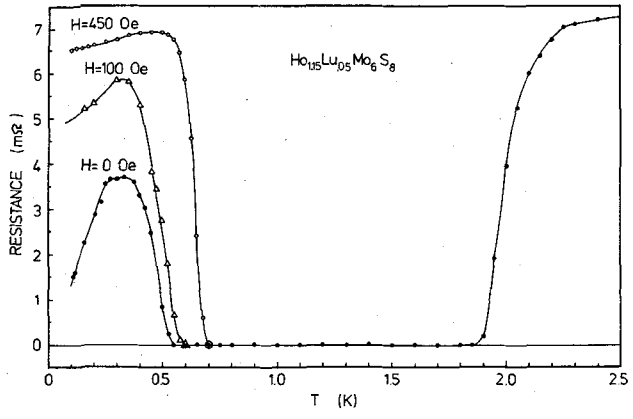

Fig. 10 : dc resistance vs temperature for $Ho_{1.15}Lu_{0.05}Mo_6S_8$. Note the linear decrease on the curve for H = 0 Oe

Before this article is concluded, a few general remarks pertinent to the problem of coexistence in these Chevrel compounds are made in the following. Long range magnetic orders in their superconducting states have now been proved in these compounds with the aid of neutron diffraction experiments. However, more experiments must be carried out in order to better understand the microscopic nature of this coexistence. At the present stage, the preparation of very homogeneous and pure samples of these compounds is an extremely difficult task. The experiments have been so far performed exclusively on carefully prepared sintered powders, and therefore the microstructure could not be properly investigated. This question would be particularly important for studies of dilute pseudoternary compounds. With regards to the magnetic states in these compounds, more detailed studies especially on the crystalline field effect in taking into account the precise symmetry around each RE ion would be indispensable, as well as a check on a possible slight change of symmetry at the magnetic phase transition. Nevertheless, this class of dense magnetic compounds provides us without question an excellent opportunity to further help our understanding of the problem of coexistence.

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