SUPERCONDUCTIVITY AND MAGNETIC ORDER

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Résumé.- Les composés supraconducteurs terres rares (TR) ternaires et pseudoternaires sont des candidats excellents pour une étude de la coexistence de la supraconductivité et l'ordre à longue portée des moments magnétiques des terres rares. Nous présentons un bref résumé des investigations récentes sur l'interaction entre la supraconductivité et l'ordre magnétique à longue portée dans les composés ternaires et pseudoternaires des TR molybdène chalcogénide et rhodium boride.

Abstract.- Superconducting ternary and pseudoternary rare earth (RE) compounds are excellent candidates in which to study the coexistence of superconductivity and long-range ordering of RE magnetic moments. Recent investigations of the interaction between superconductivity and long-range magnetic order in ternary and pseudoternary RE molybdenum chalcogenide and RE rhodium boride compounds are briefly reviewed.

1. INTRODUCTION.- Superconducting ternary compounds of rare earth (RE) ions with partially-filled 4f electron shells provide a unique opportunity to study the coexistence of superconductivity and magnetic order. Since the RE ions in these ternary compounds are distributed periodically throughout the lattice, ordering of the RE magnetic moments via the RKKY interaction is long-range in nature and characterized by a sharp magnetic ordering temperature T_M and well-defined features in the physical properties at T_M. In many of these ternary RE compounds, the exchange interaction between the conduction electron spins and RE magnetic moments is weak (the exchange interaction parameter $\mathcal{J}$ is $\sim$ 0.01 eV). This enables the compounds to retain their superconductivity even in the presence of relatively large concentrations of RE ions and results in low values of T_M that are comparable to the superconducting transition temperature T_c.

Two systems of isostructural ternary RE compounds, the rhombohedral RE molybdenum chalcogenides, $RE_xMo_6S_8$ /1/ and $RE_xMo_6Se_8$ /2/ (x = 1.0 or 1.2), and the tetragonal RE rhodium borides, $RERh_4B_4$ /3,4/, have been found to exhibit superconductivity. Ternary and pseudoternary RE compounds within these two crystal structure types have been the focus of recent investigations of the interaction between superconductivity and long-range magnetic order which are briefly reviewed. A more extensive review of some of the material discussed herein can be found elsewhere /5/.

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2. COEXISTENCE OF SUPERCONDUCTIVITY AND ANTIFERROMAGNETIC ORDER.- Coexistence of superconductivity and long-range order that is antiferromagnetic in nature has been reported for several of the rhombohedral RE molybdenum chalcogenide compounds $RE_xMo_6S_8$ /6/ and $RE_xMo_6Se_8$ (x = 1.0 or 1.2). /7-11/.

With the exception of Ce and Eu, all of the $RE_xMo_6S_8$ /1/ and $RE_xMo_6Se_8$ /2/ compounds are superconducting. The superconducting transition temperature T_c of both series of compounds exhibits a characteristic variation with RE that can be accounted for in terms of superconducting electron depairing via the exchange interaction between the conduction electron spins and the RE magnetic moments /12,13/. The Ce and Eu compounds apparently remain normal to 50 mK because of extremely large depressions of their transition temperatures due to anomalous exchange scattering associated with the Kondo effect /12/.

The onset of antiferromagnetic order in the superconducting state for $RE_{1.2}Mo_6S_8$ compounds with RE = Tb, Dy and Er was recently inferred by Ishikawa and Fischer from a feature at the magnetic ordering temperature T_M in the curve of the upper critical field vs temperature /7/. The occurrence of antiferromagnetic order in the superconducting state for $RE_xMo_6Se_8$ (x = 1.0 or 1.2) compounds with RE = Gd, Tb and Er was deduced from the simultaneous presence of a pronounced lambda-type anomaly in the specific heat and a cusp-like feature in the magnetic suscep-

-tibility at T_M /7-11/. Magnetic susceptibility measurements in the superconducting state are possible in many of the $RE_xMo_6Se_8$ compounds because they are extreme type II superconductors /14/ that permit nearly complete penetration of the magnetic fields in which the magnetization measurements were made. The types of behavior observed are exemplified by the plots of specific heat C and inverse molar magnetic susceptibility χ_M^{-1} vs temperature for $Er_{1.2}Mo_6Se_8$ that are displayed in figure 1 and 2 respectively /10/. The specific heat data of figure

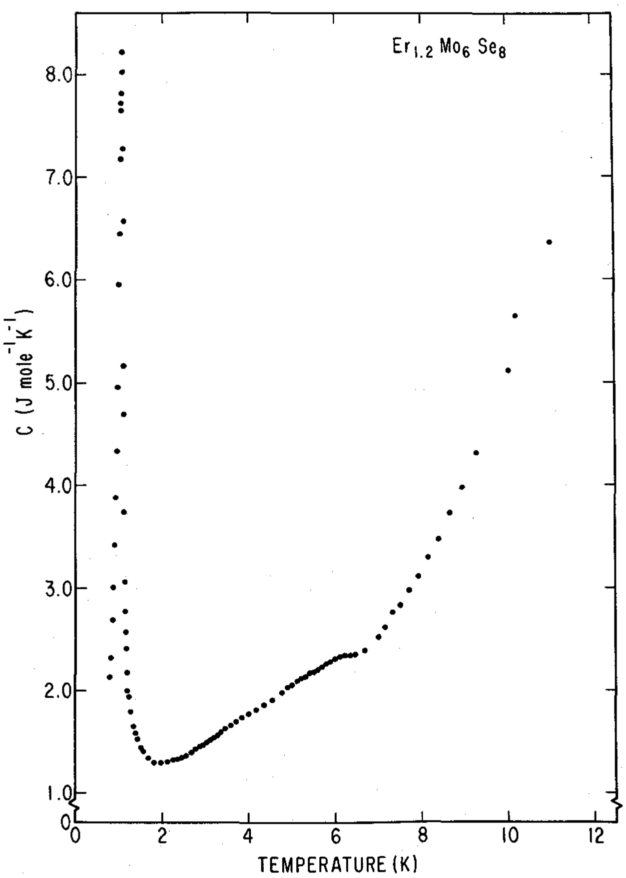

Fig. 1 : Specific heat C vs temperature for $Er_{1.2}Mo_6Se_8$ (from Ref. /10/).

1 exhibit a jump near 6 K which is associated with the superconducting transition and a remarkable lambda-type anomaly at a temperature T_λ = 1.07 K that appears to be due to long-range ordering of the Er^{3+} magnetic moments in the superconducting state. This is borne out by the cusp-like feature near T_λ in the magnetic susceptibility data of figure 2 which indicates that the long-range magnetic order is antiferromagnetic in nature. The entropy of ordering of the Er^{3+} magnetic moments conforms closely with the value corresponding to the ground state degeneracy of the Er^{3+} ions in $Er_{1.2}Mo_6Se_8$, and the magnetic field dependence of the lambda-type anomaly is consistent with antiferromagnetic order /10/.

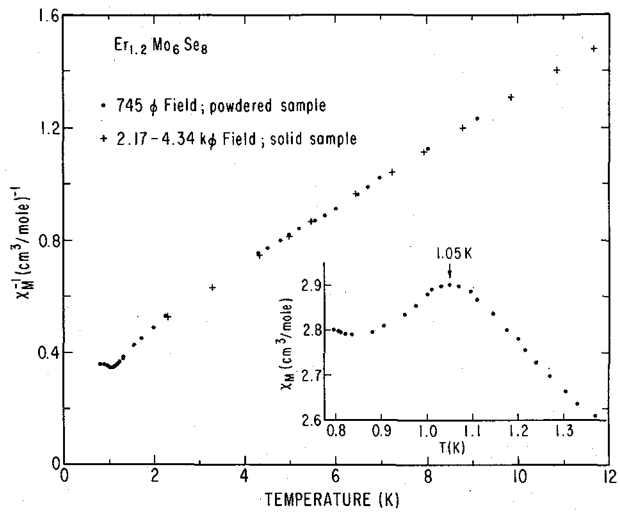

Fig. 2 : Inverse molar suceptibility χ_M^{-1} vs temperature T for $Er_{1.2}Mo_6Se_8$ (solid and powdered samples) between 0.8 and 12 K. A plot of χ_M vs T in the vicinity of the Néel temperature at 1.05 K is displayed in the inset (from Ref. /10/).

Recent powder neutron diffraction data on $Er_xMo_6Se_8$ verify that long-range ordering of the Er^{3+} magnetic moments develops at T_M but it has not yet been possible to index the magnetic Bragg reflections and thereby determine the Er^{3+} magnetic structure /15/. Calorimetric evidence for a magnetic transition in the superconducting state for $Yb_{1.0}Mo_6S_8$ was recently reported by Alekseevski et al. /16/.

3. REENTRANT SUPERCONDUCTIVITY DUE TO THE ONSET OF FERROMAGNETIC ORDER.-

3.1. Ternary rare earth compounds.- Destruction of superconductivity at a second lower critical temperature by the onset of long-range magnetic order was reported recently for *two* ternary RE compounds, $Ho_{1.2}Mo_6S_8$ /17/ and $ErRh_4B_4$ /18/. Neutron scattering experiments on $Ho_{1.2}Mo_6S_8$ /19/ and $ErRh_4B_4$ /20/ have shown that the long-range magnetic order that develops in both compounds is ferromagnetic. The compound $ErRh_4B_4$ belongs to a series of tetragonal RE rhodium borides $RERh_4B_4$ which were originally reported by Matthias and coworkers /3,4/ to have ground states that, with increasing 4f electron shell occupation number, switched from superconducting for RE = Sm and Nd, to ferromagnetic for RE = Gd, Tb, Dy and Ho, and back to superconducting for RE = Er, Tm and Lu.

Shown in figure 3 are plots of the ac magnetic susceptibility χ_{ac} and electrical resistance of $ErRh_4B_4$ as functions of temperature /18/.

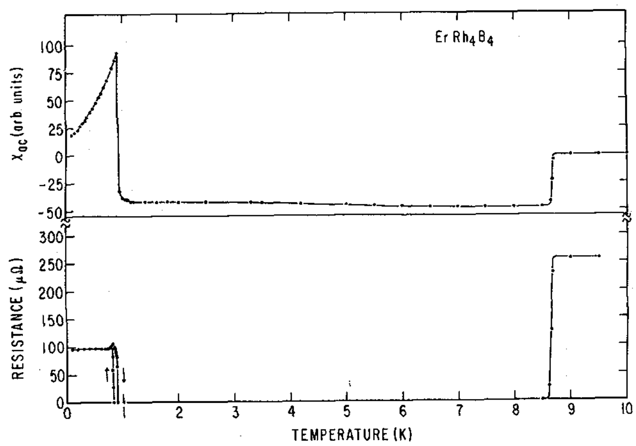

Fig. 3 : ac magnetic susceptibility χ_{ac} and ac electrical resistance vs temperature for $ErRh_4B_4$ (from Ref. /18/).

Both measurements reveal a transition to the superconducting state at T_{c1} = 8.7 K, followed by a transition back to the normal state at $T_{c2} \simeq 0.9$ K which is thermally hysteretic. In addition, χ_{ac} exhibits a large positive value just below T_{c2} and rapidly becomes less paramagnetic with decreasing temperature. The latter behavior indicates that a transition to a magnetically ordered state accompanies the superconducting to normal state transition at T_{c2}. Similar behavior or the magnetic susceptibility and electrical resistance is exhibited by $Ho_{1.2}Mo_6S_8$ /17/.

A plot of the specific heat C of $ErRh_4B_4$ and its nonmagnetic counterpart $LuRh_4B_4$ as a function of temperature T between 0.5 and 18 K is displayed in figure 4 /21/. The $ErRh_4B_4$ data reveal a specific heat jump at the upper critical temperature T_{c1} = 8.7 K followed by a pronounced lambda-type anomaly with a peak at 0.93 K near the lower critical temperature T_{c2}. Shown in the inset of figure 4 is a C vs T plot in the vicinity of T_{c2} which reveals the presence of a sharp spike-shaped feature at the peak of the lambda-type anomaly. This feature appears to be due to the coupled superconducting-ferromagnetic transition which takes place at T_{c2}. The entropy associated with the lambda-type anomaly is $\sim k_B \ln 4$, indicating that the degeneracy of the Er^{3+} J = 15/2 Hund's rule multiplet is partially lifted by the crystalline electric field, and that the ground state is a quartet or a doublet separated from another low-lying doublet excited state by less than a few degrees Kelvin. The remainder of the $k_B \ln 16$ entropy of the Er^{+} J = 15/2 Hund's rule multiplet resides in a Schottky anomaly with a peak near 11 K. Mössbauer effect /22/ high field magnetization and thermal expansion /23/ measurements have also been carried out on $ErRh_4B_4$.

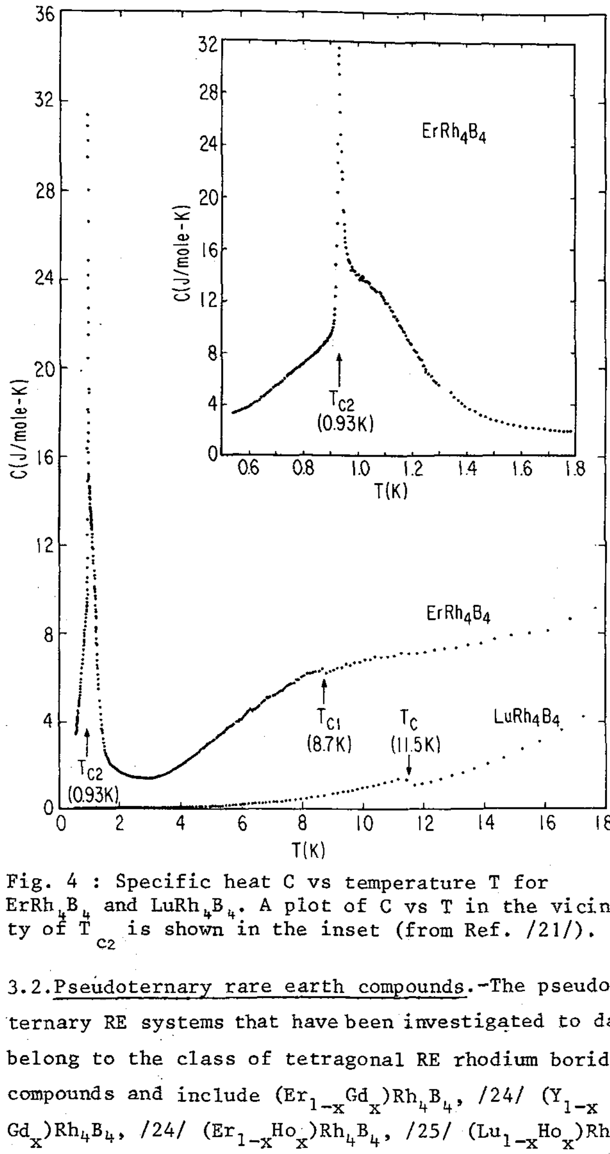

Fig. 4 : Specific heat C vs temperature T for $ErRh_4B_4$ and $LuRh_4B_4$. A plot of C vs T in the vicinity of T_{c2} is shown in the inset (from Ref. /21/).

3.2. Pseudoternary rare earth compounds.- The pseudoternary RE systems that have been investigated to date belong to the class of tetragonal RE rhodium boride compounds and include $(Er_{1-x}Gd_x)Rh_4B_4$, /24/ $(Y_{1-x}Gd_x)Rh_4B_4$, /24/ $(Er_{1-x}Ho_x)Rh_4B_4$, /25/ $(Lu_{1-x}Ho_x)Rh_4B_4$, /26/ and $(Er_{1-x}Tm_x)Rh_4B_4$ /27/.

The $(Lu_{1-x}Ho_x)Rh_4B_4$ pseudoternary system, whose low temperature phase diagram is shown in figure 5, /26/ exhibits many of the features that are common to all of the $RERh_4B_4$ pseudoternary systems that have been studied. Figure 5 shows that the upper and lower critical temperatures T_{c1} and T_{c2} and the magnetic ordering temperature T_M converge at a critical concentration x_{cr} = 0.92 below which re-entrant superconductive behavior occurs and above which only magnetic ordering occurs.

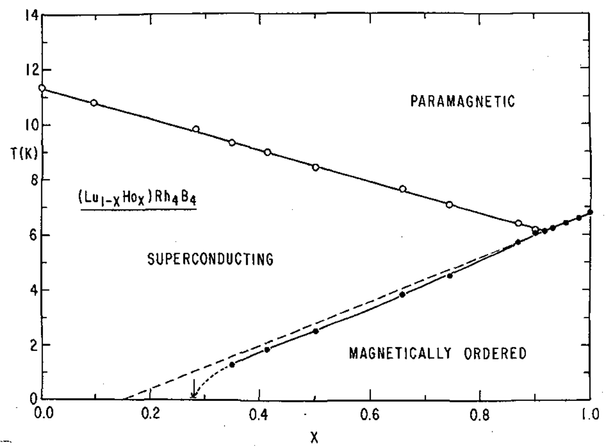

Fig. 5 : Low temperature phase diagram for the pseudoternary system $(Lu_{1-x}Ho_x)Rh_4B_4$ (from Ref. /26/)

The ac magnetic susceptibility measurements that were employed to establish the low temperature phase diagram for $(Lu_{1-x}Ho_x)Rh_4B_4$ do not reveal whether the curve of T_{c2} vs x actually coincides with the curve of T_M vs x for $x < x_{cr}$. However, low temperature heat capacity data for a $(Lu_{0.5}Ho_{0.5})Rh_4B_4$ compound indicate that T_{c2} and T_M for $x < x_{cr}$ are coincident, or nearly so. The low temperature heat capacity data for $(Lu_{0.5}Ho_{0.5})Rh_4B_4$ and the end-member $LuRh_4B_4$ and $HoRh_4B_4$ compounds are shown in figure 6 /26/. The data for $(Lu_{0.5}Ho_{0.5})Rh_4B_4$ exhibit a

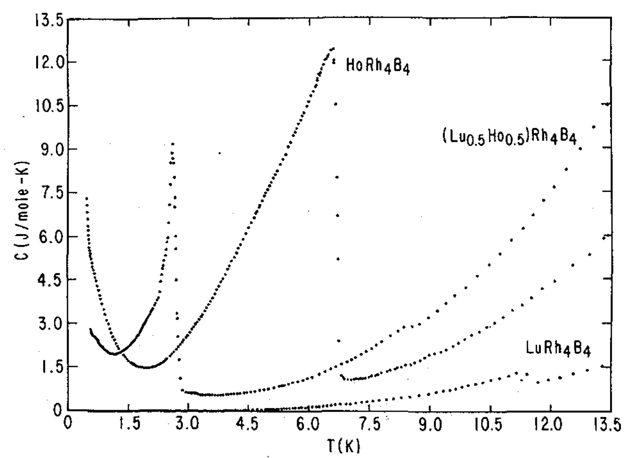

Fig. 6 : Specific heat C vs temperature T for $LuRh_4B_4$, $HoRh_4B_4$ and $(Lu_{0.5}Ho_{0.5})Rh_4B_4$ (from Ref./26/)

specific heat jump at T_{c1}, a sawtooth-shaped feature associated with long-range magnetic order that occurs at a temperature $T_M \approx T_{c2}$, and a low temperature tail which is apparently the high temperature portion of Ho nuclear Schottky anomaly. The latter two features are similar to those that appear in the heat capacity of the ferromagnetic $HoRh_4B_4$ compound. An additional feature of the heat capacity data for $(Lu_{0.5}Ho_{0.5})Rh_4B_4$ is the spike-shaped anomaly at $T_M \approx T_{c2}$ that is superimposed on the sawtooth shaped feature /26,28/. The spike-shaped anomaly resembles that observed for $ErRh_4B_4$ and, similarly, is apparently due to the coupled superconducting-ferromagnetic transition since it does not appear in the heat capacity data for $HoRh_4B_4$. Since T_{c2} and T_M are coincident, the reduction of the curve of T_{c2} vs x relative to the linearly extrapolated curve of T_M vs x for $x < x_{cr}$ (indicated by the dashed line in figure 5), is consistent with a reduced value of the conduction electron susceptibility $\chi_e(q)$ for $q < k_F$ in the superconducting state (k_F is the Fermi momentum) /29/.

4. CONCLUDING REMARKS.- Superconducting ternary and pseudoternary compounds of RE ions with partially-filled 4f electron shells are excellent candidates in which to study the interaction between superconductivity and long-range ordering of RE magnetic moments. The experiments have thus far revealed the development of long-range magnetic order in the superconducting state, the coexistence of superconductivity and long-range antiferromagnetic order, the destruction of superconductivity at a second lower critical temperature T_{c2} by the onset of long-range ferromagnetic order, and a new spike-shaped specific heat anomaly at T_{c2} which is apparently associated with the coupled superconducting-ferromagnetic transition. It can be anticipated that the experiments reviewed herein and future investigations on superconducting ternary and pseudoternary RE compounds will make it possible to establish the criteria for, and critically test theories of /29/, the coexistence of superconductivity and various types of ordered magnetic structures.

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