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DESTRUCTION OF PRESSURE-INDUCED SUPERCONDUCTIVITY BY LONG-RANGE ANTIFERROMAGNETIC ORDER IN $Tm_2Fe_3Si_5$

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Reentrant superconductivity has been detected in a well characterized sample of $Tm_2Fe_3Si_5$ by ac susceptibility measurements under applied pressure. The superconducting transition temperature displays a pronounced, non-linear behavior under pressure, starting at low pressures with an increase which is among the largest known for any compound (dT_{c1}/dp = 0.47 K/kbar). The magnetic transition temperature is relatively pressure independent.

There has been sustained theoretical and experimental interest in magnetic perturbations of superconductors since the early studies of magnetic impurities in superconductors, and more recently with the advent of ternary materials such as RRh_4B_4, RMo_6Se_8, and RMo_6S_8 (R = rare earth) which exhibit superconductivity even in the presence of a regular sublattice of magnetic ions [1]. These latter materials exhibit a rich variety of behavior including the destruction of superconductivity by the onset of long range ferromagnetic order and coexistence of superconductivity with long range antiferromagnetic order. Many new ternary systems have been discovered [2], but often only the superconducting transition temperatures are reported. The ternary iron silicides, $R_2Fe_3Si_5$ (R = Sc, Y, Lu and Tm), however, have received much attention due to the high superconducting transition temperatures [3,4] (6.2 K) exhibited even in the presence of 30% iron and due to the absence of superconductivity in the isostructural and isoelectronic $R_2T_3Si_5$ (T = Ru, Os) compounds [5]. These superconducting materials exhibit a variety of unusual behavior including high sensitivity to non-magnetic impurities, large non-linear effects of pressure on T_c and anomalous non BCS-like heat capacity in the superconducting state [6,7].

Braun and Segre reported reentrant superconductivity in $Tm_2Fe_3Si_5$ based on ac susceptibility measurements [8], but the superconducting transition was not complete before it was destroyed by the onset of long range magnetic order associated with the Tm ions. Recent neutron diffraction measurements on $Tm_2Fe_3Si_5$ confirmed antiferromagnetic ordering of the Tm ions in this compound [9]. Since no other stoichiometric material is known in which superconductivity is destroyed by the onset of antiferromagnetic order and since the concentration of magnetic Tm ions is 20% in this compound which is higher than the concentration of magnetic rare earths in any other superconductor, the results of Braun and Segre appear all the more significant. In order to help understand superconductivity in this material, we have performed ac susceptibility measurements on $Tm_2Fe_3Si_5$ under high pressure which confirm the observation of reentrant superconductivity in this material, but only under applied pressure for our sample. These results establish $Tm_2Fe_3Si_5$ as the first stoichiometric, ordered system in which superconductivity is destroyed by the onset of antiferromagnetic order.

Low temperature heat capacity [7,10], susceptibility [11,12], Mössbauer [11-14], alloying [5,6], neutron diffraction [9,15,16], and pressure studies [5,6] have been performed recently on ternary iron silicides of the type $R_2Fe_3Si_5$ (R = Sc, Y, Sm, Gd-Lu). Recent low temperature neutron diffraction measurements on $Tm_2Fe_3Si_5$ are consistent with an antiferromagnetic arrangement of the Tm ions, with no evidence of a magnetic moment associated with the iron ions and no evidence of a ferromagnetic component to the structure [9]. These results are in accord with previous neutron diffraction studies on $Tb_2Fe_3Si_5$ and $Er_2Fe_3Si_5$ which exhibit related, complex antiferromagnetic order [15,16]. Previous dc magnetic susceptibility measurements have also indicated antiferromagnetic order for $R_2Fe_3Si_5$ with R = Sm, Gd-Tm [11,12]. Low temperature heat capacity measurements indicate that Tm is an effective

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spin 1/2 ion in $Tm_2Fe_3Si_5$ [10]. Mössbauer measurements show that there is no long lived moment on the iron atoms [11,14], in agreement with other measurements.

The experiments reported here were performed on the same ingot of $Tm_2Fe_3Si_5$ used in a previous heat capacity study [10]. Electron microprobe and powder x-ray diffraction measurements indicate that this sample contains less than 0.5% secondary phases. In order to identify the important impurity phases, a search of the Er-Fe-Si ternary system was attempted which revealed several new ternary compounds [17], none of which is superconducting above 1 K. Moreover, it is unlikely that more than one ternary compound in the Tm-Fe-Si system is superconducting, which supports association of all of the observed properties with the 2:3:5 phase. The ac susceptibility measurements at low temperatures and under applied pressures up to 23 kbar on $Tm_2Fe_3Si_5$ were performed in a standard Be-Cu piston cell [18]. The applied pressure was determined at low temperatures using a superconducting Sn manometer [19].

Figure 1 shows χ_{ac} vs temperature for $Tm_2Fe_3Si_5$ for five applied pressures. At 1 kbar the change in the susceptibility is quite small over this temperature range. A cusp associated with antiferromagnetic order is visible at 1.1 K and a broad, weak minimum in the susceptibility is evident near 1.5 K. Based on features of this magnitude reentrant superconductivity was reported previously in this compound [8]. By 3 kbar, strong diamagnetism is observed from 1.8 K to 1.1 K where the superconducting state is destroyed at a temperature near the Néel temperature. Under higher pressures, T_{c1} increases up to a maximum of 3.13 K at 8.9 kbar and a clear hysteresis is observed at the reentrant temperature, 1.2 K. This hysteresis indicates that at this pressure, superconductivity is destroyed by a first order phase transition.

At still higher pressures, T_{c1} decreases sharply until bulk superconductivity is no longer observed above 21 kbar, although the behavior of χ_{ac} at this pressure still indicates some trace of superconductivity, perhaps due to strains within the sample. The pressure-temperature phase diagram is presented in Fig. 2. The spectacular pressure dependence of T_{c1} (dT_{c1}/dp = 0.47 K/kbar at 3 kbar), is among the largest known for any compound and is 25 times larger than values typical of most superconductors, for example the RRh_4B_4 ternaries. Indeed, the only other systems in which pressure effects of this magnitude are observed are some of the Chevrel phase compounds [20], α-U [21] and the lanthanum chalcogenides [22] where structural instabilities and/or structural transformations are believed responsible for the dramatic pressure effects.

In searching for causes of this striking pressure dependence, one may conclude that the effect of pressure on T_{c1} is unrelated to the magnetic order on the Tm sites by comparing the behavior of $Tm_2Fe_3Si_5$ under pressure to that of the isostructural superconductors $Y_2Fe_3Si_5$, $Lu_2Fe_3Si_5$, and $Sc_2Fe_3Si_5$, listed here in order

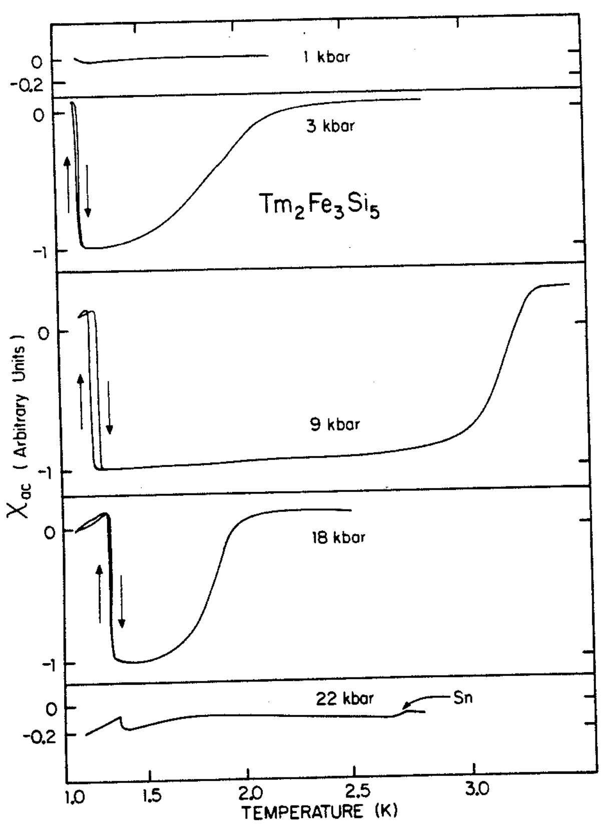

Fig. 1. ac susceptibility for $Tm_2Fe_3Si_5$ at five applied pressures. The superconducting transition of a Sn manometer is indicated at 22 kbar.

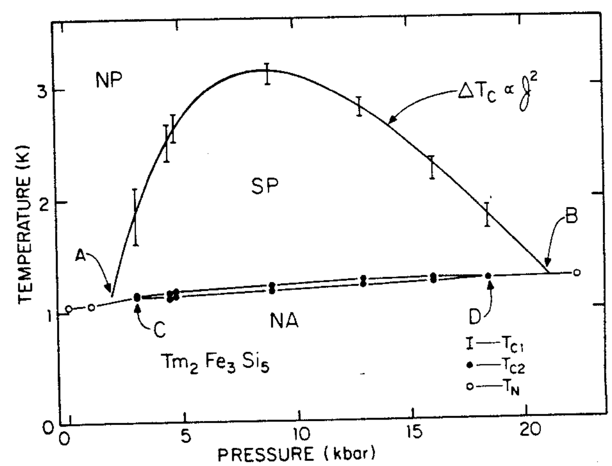

Fig. 2. The low temperature phase diagram for $Tm_2Fe_3Si_5$. Critical temperatures for the onset of superconductivity (I, T_{C1}), the destruction of superconductivity (•, T_{C2}) and the onset of long-range antiferromagnetic order (O, T_N) are indicated. The three states, normal paramagnetic (NP), superconducting (SP), and normal antiferromagnetic (NA) are also shown. The solid lines through the data provide a guide to indicate the phase boundaries.

of decreasing unit cell volume [3,6]. The effect of pressure on the superconducting transition temperature of $Y_2Fe_3Si_5$ [6] is similar to the results reported here for $Tm_2Fe_3Si_5$, except that there is no magnetism associated with Y in the former compound. The Lu and Sc compounds exhibit a monotonic depression of T_c with applied pressure [6], consistent with an internal "chemical pressure" due to their smaller unit cell volume. This internal "chemical pressure", a model proposed by Segre [5], results in a T_c vs pressure behavior of the Lu and Sc compounds which corresponds to the high pressure side of the maximum observed in T_{c1} in Fig. 2. Therefore, the pressure dependence of T_{c1} in $Tm_2Fe_3Si_5$ must be considered a universal feature of this class of compounds and not related to the magnetic nature of the Tm ions.

As previously mentioned, other materials which exhibit a large non-linear pressure dependence of T_{c1} often undergo a structural transformation. The possibility of a significant structural transformation in $Tm_2Fe_3Si_5$ at ambient pressure is eliminated by low temperature neutron diffraction experiments [9]. Indeed, neutron diffraction studies on $Er_2Fe_3Si_5$ and $Tb_2Fe_3Si_5$ plus X-ray diffraction measurements on $Sc_2Fe_3Si_5$ indicate that there are no structural changes in any of these compounds down to their magnetic or superconducting state [7,15,16]. Since all scattering experiments have been done at ambient pressure, the possibility of a pressure-induced structural transformation still remains to be investigated. Low temperature neutron scattering experiments under high pressure conditions are planned.

These experiments will also address the question of whether the antiferromagnetic state determined at ambient pressure [9] remains unchanged by the application of hydrostatic pressure. The smooth and small variation of T_N with pressure (see Fig. 2) argues against any significant or sudden change in the nature of the magnetic state with pressure. From our data, the possibility of a new, distinct magnetic phase, perhaps with a ferromagnetic component, seems remote. However, this question must be decided by direct experimental means since the destruction of superconductivity by the onset of long range antiferromagnetic order has not been unambiguously identified in any other stoichiometric compound. Indeed, this is the only ternary system with two multicritical points in an accessible range (see points A and B in Fig. 2). Thermal hysteresis of about 50 mK is observed at T_{c2} between 4.4 and 16 kbar (points C and D in Fig. 2) and is roughly constant in this range of applied pressure suggesting that the superconducting to antiferromagnetic transition is of first order in this region. This may indicate the presence of an intermediate oscillatory phase where long range magnetic order and superconductivity coexist, as has been observed in the ferromagnetic superconductors $ErRh_4B_4$ and $HoMo_6S_8$ [1]. Little or no thermal hysteresis is observed in the susceptibility at 3 and 18 kbar, however, indicating a second order phase transition in this region. This result is in accord with recent theory which predicts there should be no "tetra-critical" points in the phase diagrams of reentrant superconductors, that is no coexistence phase near the tri-critical points [23]. The reentrant behavior observed here is not in accord with most current theories on antiferromagnetic superconductors which predict a second order transition to a coexisting superconducting-antiferromagnetically ordered state [24]. The reentrant transition at T_{c2} associated with the onset of antiferromagnetic order is of considerable interest in several respects. The net magnetization which provides the principle coupling between ferromagnetic order and superconductivity is absent in this compound and yet, many of the earmarks of the ferromagnetic superconductors are reproduced here. For example, we observe a sharp, hysteretic transition from the superconducting to the magnetically ordered state. This provides a serious constraint on theories of antiferromagnetic superconductors and may eliminate some models.

The unique results reported here are: (i) clear evidence for bulk superconductivity in a stoichiometric compound containing 20 at% magnetic rare-earth element, (ii) the destruction of superconductivity by long-range antiferromagnetic order on an isoatomic, ordered sublattice, and (iii) a ternary compound with two multicritical points in a readily accessible portion of the pressure-temperature phase diagram.

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