Low-temperature heat capacity of superconducting ternary iron silicides

C. B. Vining and R. N. Shelton
Ames Laboratory and Department of Physics, Iowa State University, Ames, Iowa 50011

H. F. Braun and M. Pelizzone
Département de Physique de la Matière Condensée, Université de Genève, Ch-1211 Genève 4, Switzerland
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The low-temperature heat capacity of superconducting ternary iron silicides $Lu_2Fe_3Si_5$, $Sc_2Fe_3Si_5$, and $Y_2Fe_3Si_5$ has been measured, revealing several anomalous properties of the superconducting state of these materials. These materials show a large linear term in the superconducting heat capacity and a reduced normalized jump in the specific heat at T_c. A two-band model is proposed to explain these properties and previously reported anomalous properties of superconducting ternary iron silicides.

INTRODUCTION

Ternary superconductors, particularly the Chevrel phase compounds and the rhodium borides, have been extensively studied in recent years.[1,2] A major motivation in this work has been the investigation of the competition between superconductivity and magnetism made possible by the presence of a sublattice of magnetic rare-earth atoms. The discovery of $Sc_5Co_4Si_{10}$ with a superconducting transition temperature (T_c) of 4.9 K demonstrated that relatively high T_c's may be found among compounds containing 3*d* transition elements as intrinsic constituents.[3]

Among binary-ion compounds only U_6Fe ($T_c=3.9$ K) (Ref. 4) and Th_7Fe_3 ($T_c=1.86$ K) (Ref. 5) are superconducting above 1 K. Recently five ternary compounds containing iron as the transition metal [$M_2Fe_3Si_5$ with M=Lu,Sc,Y,Tm (Refs. 6 and 7) and $LaFe_4P_{12}$ (Ref. 8)] have been reported superconducting. The ternary-iron silicides, $M_2Fe_3Si_5$ were first reported superconducting by Braun in 1980.[6] The properties of these materials are anomalous in several respects: (i) The effect of pressure on T_c is among the largest known ($dT_c/dp=-7\times10^{-5}$ K/bar for $Lu_2Fe_3Si_5$ and $Sc_2Fe_3Si_5$ and $dT_c/dp=33\times10^{-5}$ K/bar for $Y_2Fe_3Si_5$) (Ref. 9); (ii) the rapid depression of T_c with nonmagnetic impurities (T_c drops below 1 K for 15% Sc substituted for Lu in $Lu_2Fe_3Si_5$) (Ref. 10); (iii) reentrant superconductivity has been reported in $Tm_2Fe_3Si_5$ (Ref. 7); (iv) there is no magnetic moment on the iron in this structure as indicated by Mössbauer spectroscopy[11–13]; (v) a commensurate-incommensurate magnetic transition has been observed in antiferromagnetic $Tb_2Fe_3Si_5$.[14]

The low-temperature heat capacity for the compounds $Lu_2Fe_3Si_5$, $Sc_2Fe_3Si_5$, and $Y_2Fe_3Si_5$ is reported here as part of a systematic study of the low-temperature properties of $M_2Fe_3Si_5$ materials (M=Sm, Gd-Lu, Sc, and Y). The low-temperature heat capacity of the magnetic rare-earth compounds will be reported elsewhere.

SAMPLE PREPARATION AND CHARACTERIZATION

Samples of $Lu_2Fe_3Si_5$, $Sc_2Fe_3Si_5$, and $Y_2Fe_3Si_5$ of 3–4 g each were prepared by arc-melting stoichiometric mixtures of high-purity elements in a Zr-gettered argon atmosphere. The resulting ingots were then turned over and remelted at least six times to promote homogeneity. The samples were then sealed in quartz ampoules with about 300 Torr of argon and annealed at 1250 °C for five days followed by seven days at 800 °C. The resulting ingots were shiny, heavily faceted, hard, and brittle with cracks over much of the surface.

Powder x-ray diffraction confirms the presence of the 2:3:5 phase (space group *P*4/*mnc*) with lattice parameters in agreement with those reported by Braun.[6] Low-temperature powder x-ray diffraction indicates no structural transformation above 30 K. In each sample the x-rays show only one or two very weak lines not indexable to the 2:3:5 structure which are attributed to small amounts of impurities. Optical microscope investigations indicate large grains of 100–200 μm with small amounts of impurities along the grain boundaries. Microprobe results indicate two major impurities of approximate compositions FeSi and MFe_3Si_7. Total impurities are estimated to be about 2% by volume in each sample.

Low-frequency ac inductance measurements indicate superconducting transitions at 6.3, 4.4, and 1.7 K for $Lu_2Fe_3Si_5$, $Sc_2Fe_3Si_5$, and $Y_2Fe_3Si_5$, respectively, in agreement with previous results.[6,9] The transitions are sharp ($\Delta T_c = 0.2$ K) and consistent with bulk superconductivity.

Magnetic susceptibility measurements from 5 to 250 K on a piece of the sample of $Lu_2Fe_3Si_5$ used in the heat-capacity measurements indicate a paramagnetic susceptibility consistent with an upper limit of 14 ppm free iron. Similar measurements on samples of $Sc_2Fe_3Si_5$ and $Y_2Fe_3Si_5$ which were not used in the heat-capacity measurements indicate upper limits of 38 and 30 ppm free iron, respectively, in these samples. These data are shown in Fig. 1.

In addition to the above samples, a series of five samples $Sc_2Fe_{3+\delta}Si_5$ ($\delta = -0.5, -0.1, 0.0, 0.1, 0.5$) not used in the heat-capacity measurements were prepared to study the effect of stoichiometry on the superconducting properties. These samples were prepared with special attention to the relative amounts of Fe in each sample. From a master ingot of Sc_2Si_5, samples of $Sc_2Fe_{2.5}Si_5$ and $Sc_2Fe_{3.5}Si_5$ were prepared by adding the appropriate amounts of Fe. The remaining three samples ($\delta = -0.1, 0.0, 0.1$) were prepared by mixing appropriate amounts of these two samples. The superconducting transition temperatures of these five samples are presented in Fig. 2, together with the T_c of the sample of $Sc_2Fe_3Si_5$ used in the heat-capacity study. X rays on the off-stoichiometry samples ($\delta \neq 0.0$) indicate increasing amounts of impurities with increasing $|\delta|$. The rapid depression of T_c and increased impurities with off stoichiometry indicate even a few percent of impurities can be readily identified. The results of x-ray diffraction, microprobe, T_c measurements, and effects of stoichiometry all indicate no more than a few percent impurities in the samples used in the heat-capacity measurements. The general high quality of the samples used in this study, particularly the samples of $Lu_2Fe_3Si_5$ and $Sc_2Fe_3Si_5$, and the extensive characterization of these samples play a major role in the discussion of the results below.

EXPERIMENTAL DETAILS

Low-temperature heat-capacity measurements were performed using a semiadiabatic heat pulse-type calorimeter equipped with a mechanical heat switch, a circulating ^4He pot and a circulating ^3He pot. Mechanical noise introduced while operating the ^3He system prohibited accurate data acquisition below 1 K during the measurements, limiting the usable temperature range to 1.2—30 K. This problem has since been corrected extending the usable temperature range to at least 0.5 K.

The sample holder consists of gold-plated copper in a clamp arrangement, providing good mechanical and thermal contact between the sample and the sample holder. The sample holder is supported by a rigid, thin-walled, low—thermal-conductivity nylon support providing good mechanical stability. A mechanical heat switch and thermal shield with a heater provide ambient temperature control. A four-probe method was used to simultaneously measure the current and voltage during each heat pulse of a 1000-Ω Pt-W heater on the sample holder. The duration of the heater pulse is measured with a commercial digital timer. The determination of the total heat applied to the sample is believed to introduce no more than 0.1% error to the final heat capacity.

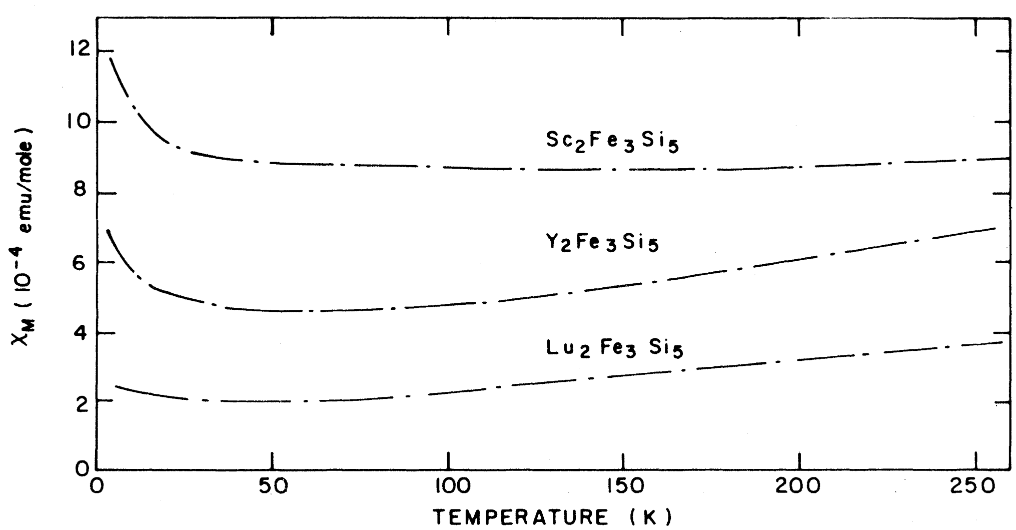

FIG. 1. Magnetic susceptibility for $Sc_2Fe_3Si_5$, $Y_2Fe_3Si_5$, and $Lu_2Fe_3Si_5$. See text for details.

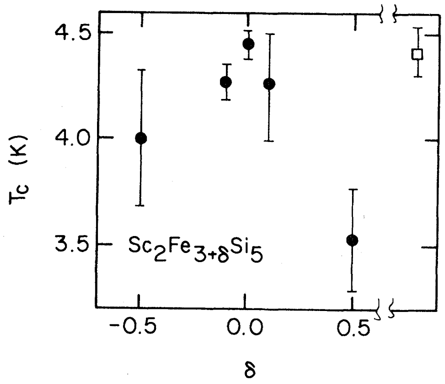

FIG. 2. Superconducting transition temperatures (●) of $Sc_2Fe_{3+\delta}Si_5$ compounds. Error bars indicate width of the transition into the superconducting state. The transition temperature for the sample of $Sc_2Fe_3Si_5$ used in the heat-capacity measurements is indicated at the right (□).

The thermometry consists of a germanium resistance thermometer (GRT) and a commerically available potentiometric conductance bridge. The GRT was selected for its extended usable temperature range (0.3—30 K) and calibrated in this laboratory in the range 0.9—30 K against a GRT known for its stablity and reliability as a secondary standard. The calibration procedure and equipment is described in Ref. 15. A second calibration, overlapping this one, was performed from 0.3 —2.0 K against a GRT calibrated in this range by the manufacturer. The GRT thermometry is believed accurate to at least ± 5 mK at 20 K and ± 1 mK below 4 K. The temperature change during a heat pulse is determined by monitoring the GRT conductance on a strip-chart recorder. This graphical procedure is believed to be the principal source of random error in these measurements.

As a check of the equipment and procedures used, several runs were performed to determine the heat capacity of the addenda (sample holder, thermometer, heater, and GE 7031 varnish) and a piece of high-purity copper. The resulting overall precision in each run and agreement between different runs was typically better than 0.5%. After correcting for the addenda, the precision of the data on copper was better than 1% and yielded $\gamma = 0.688$ mJ/mole K^2 and $\Theta_D = 345$ K, in good agreement with the corresponding values for the copper reference equation.[16]

RESULTS

The low-temperature heat capacities of $Lu_2Fe_3Si_5$, $Sc_2Fe_3Si_5$, and $Y_2Fe_3Si_5$ are shown in Figs. 3—5, respectively, where C/T is plotted against T^2 in the usual manner. A jump in the heat capacity at 6.3, 4.4, and 1.7 K for $Lu_2Fe_3Si_5$, $Sc_2Fe_3Si_5$, and $Y_2Fe_3Si_5$, respectively, indicates the transition into the superconducting state. Deviations from linearity above T_c, especially in $Lu_2Fe_3Si_5$, are apparent. In

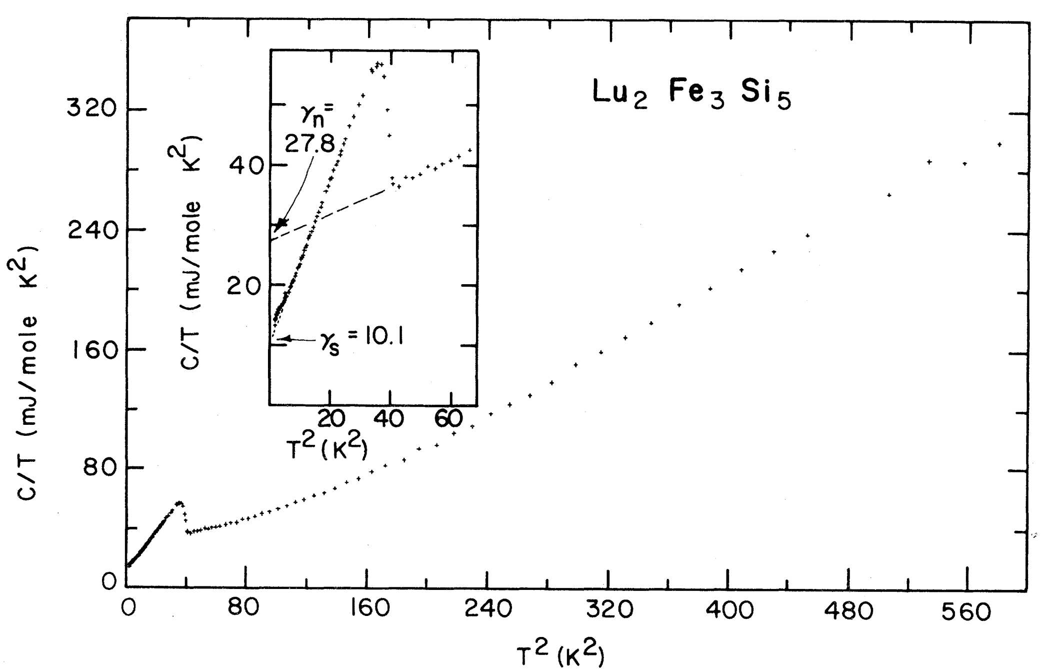

FIG. 3. C/T vs T^2 for $Lu_2Fe_3Si_5$. The inset indicates the coefficient of the linear term in the heat capacity for the normal state (γ_n) and the superconducting state (γ_s), in mJ/mole K^2.

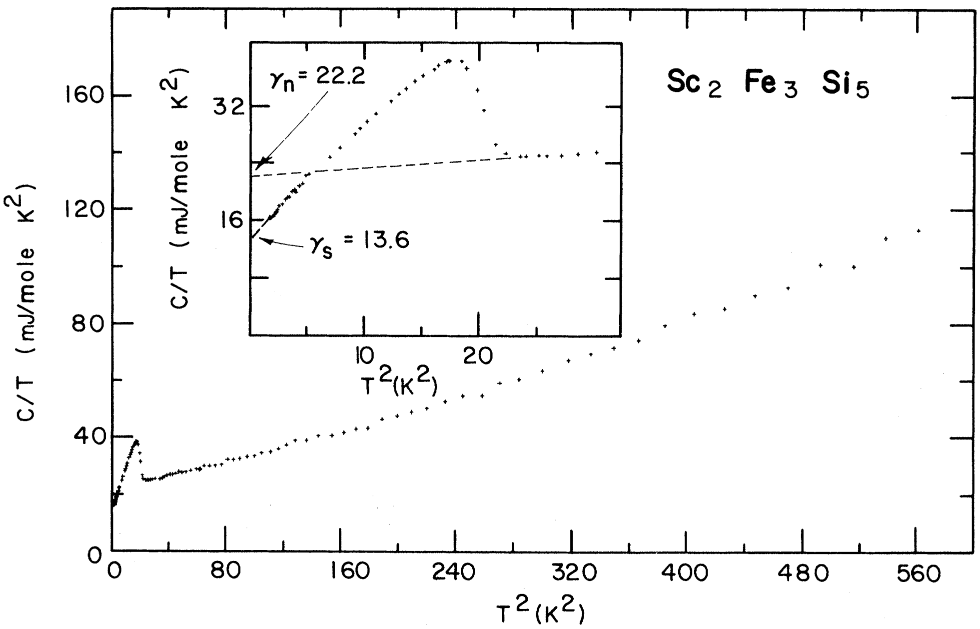

FIG. 4. C/T vs T^2 for $Sc_2Fe_3Si_5$. The inset indicates the coefficient of the linear term in the heat capacity for the normal state (γ_n) and the superconducting state (γ_s), in mJ/mole K^2.

each case the data were fit in the temperature range from above T_c to 18 K to $C=\gamma_n T+\beta_n T^3+\alpha_n T^5$ with a root-mean-square deviation of about 1% (see Table I). In each case the lattice contribution ($\beta_n T^3+\alpha_n T^5$) represents less than 20% of the total heat capacity at T_c. In the case of $Lu_2Fe_3Si_5$ the T^5 term is quite large, contributing 13% of the total heat capacity at 10 K. The rapid variation of the lattice contribution and the higher T_c (6.3 K) contribute somewhat smaller and larger values, respectively, than the values resulting from the fit. No such discrepancy exists for $Sc_2Fe_3Si_5$, where the normal

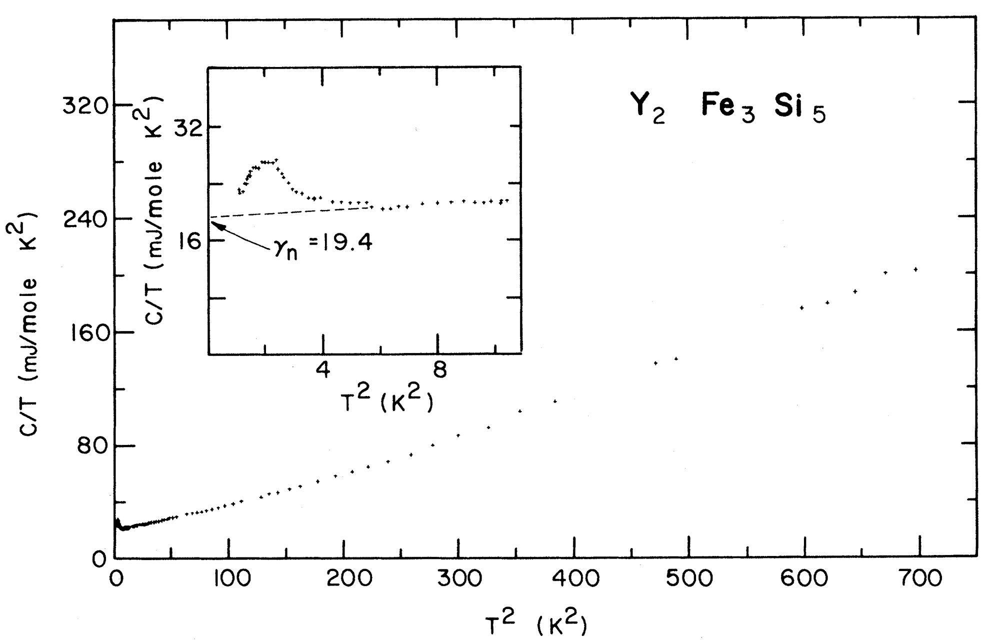

FIG. 5. C/T vs T^2 for $Y_2Fe_3Si_5$. The inset indicates the coefficient of the linear term in the heat capacity for the normal state (γ_n) in mJ/mole K^2.

TABLE I. Superconducting and normal properties of ternary iron silicides.

	Units	$Lu_2Fe_3Si_5$	$Sc_2Fe_3Si_5$	$Y_2Fe_3Si_5$
T_c	K	6.25 ± 0.15	4.46 ± 0.2	1.68 ± 0.25
γ_n	mJ/mole K^2	27.8	22.2	19.4
β_n	mJ/mole K^4	0.170	0.110	0.165
α_n	mJ/mole K^6	7.97×10^{-4}	8.82×10^{-5}	1.77×10^{-4}
Θ_D	K	485	561	490
ΔC	mJ/mole K	173.0	80.3	25.4
$\Delta C/\gamma_n T_c$		0.99	0.81	0.78
γ_s	mJ/mole K^2	10.14	13.6	
β_s	mJ/mole K^4	1.346		
$N(0)$	states/eV atom spin	0.59	0.47	0.41
λ		0.51	0.45	0.39
MW	g/mole	657.9	397.9	485.8

state data is more well behaved (i.e., the T^5 contribution is smaller) and T_c is lower.

The jump in the specific heat at T_c is sharp for $Lu_2Fe_3Si_5$ ($\Delta T_c=0.3$ K) and $Sc_2Fe_3Si_5$ ($\Delta T_c=0.35$ K). The jump at T_c for $Y_2Fe_3Si_5$ is relatively broad ($\Delta T_c=0.5$ K) with significant contributions to $C(T)$ from the superconducting state as high as 2 K. The somewhat lower value of T_c than previously reported[6] and the broadened transition into the superconducting state suggests the $Y_2Fe_3Si_5$ sample is somewhat lower in quality than the other two samples. In each case the normalized jump in the heat capacity at T_c, $\Delta C/\gamma_n T_c$, is significantly reduced from the BCS value of 1.43 (see Table I), being less than 60% of the BCS value for $Sc_2Fe_3Si_5$ and $Y_2Fe_3Si_5$. Electron-phonon coupling constants calculated using McMillan's formula[17] with $\mu^*=0.1$ (Table I) indicate these materials are intermediate-coupled superconductors.

Below T_c the heat capacity of $Lu_2Fe_3Si_5$ is remarkably simple (see inset Fig. 2). From 2.4 to 6 K the data can be described by $C=\gamma_s T+\beta_s T^3 =10.14T=1.346T^3$ mJ/mole K to within experimental error (0.7%). The linear term here is about 35% of the linear term in the normal state. Below 2.4 K a small anomaly consistent with 1–2% of impurities entering a superconducting state is evident. The heat capacity of $Sc_2Fe_3Si_5$ below T_c similarly shows a large linear term (see inset Fig. 3). Extrapolation of the lowest temperature data for $Sc_2Fe_3Si_5$ indicate $\gamma_s=13.6$ mJ/mole K^2 or 61% of the normal-state coefficient of the linear term ($\gamma_n=22.2$ mJ/mole K^2). The data on $Y_2Fe_3Si_5$ do not extend sufficiently below the T_c of this sample to permit estimating γ_s; however, entropy matching considerations suggest $\gamma_s\neq0$ in this case also.

DISCUSSION

The anomalously large T^5 contribution observed in the normal state heat capacities of these materials, especially in $Lu_2Fe_3Si_5$, suggests a rather complex phonon density of states. Deviation from T^3 in the lattice contribution to the heat capacity has been reported for other ternary superconductors[18,19] and may be a rather general consequence of the complex phonon density of states which may be expected from the complex crystal structures of these materials.

More notable are the results for measurements in the superconducting states of these materials. The reduced normalized jump at T_c and the large linear term below T_c, evident in these data, are quite unusual. There are several possible origins for a linear term in the superconducting specific heat and a reduced normalized jump at T_c: (i) the presence of bulk amounts of normal impurities or large inhomogeneities, (ii) presence of small amounts of impurities with a large γ, (iii) a gapless or mixed superconducting state induced by some pair breaking mechanism, or (iv) the existence of a region (or regions) of the Fermi surface which does not participate in superconductivity. We will consider each of these broad catergories in turn.

The rather extensive characterizations of the samples discussed above serve to address (i) and (ii). Estimating conservatively there are at most 5% impurities in any of these samples. Further, the microprobe results indicate those impurities are concentrated at the grain boundaries and are not incorporated into the 2:3:5 phase matrix. The sharpness of the transition into the superconducting state as indicated in both ac inductance and heat-capacity measurements indicates good sample homogeneity, ruling out (i) above.

Attributing γ_s in $Lu_2Fe_3Si_5$ to impurities of 5% of the material yields a $\gamma_{imp}=0.31$ mJ/g K^2. This is much larger than the γ of any of the elements, except α-Mn ($\gamma=0.32$ mJ/g K^2).[20] This comparison becomes worse, indicating an even larger, γ_{imp} for the case of $Sc_2Fe_3Si_5$ or if impurities constitute less than 5% of the material, as is very likely. Thus (ii) leads to unreasonable estimates for the heat capacity of the supposed impurities. Turning now to (iii), several sources of pair breaking are plausible in view of the large concentration of Fe present in these materials. However, the magnetic susceptibility measurements shown in Fig. 1 indicate paramagnetic impurities are present in concentrations too low to play a major role in the superconducting properties of these materials. Regardless of the source of the pair breaking, however, a large amount of pair breaking would be required to induce the large linear terms observed. This would imply a T_c in the absence of pair breaking at least several degrees higher than observed in these materials. No evidence of larger T_c's has been found in our work, nor reported in the literature. This implies the source of pair breaking would have to be intrinsic to the material and nearly independent of preparation technique. The absence of a moment on the iron atoms as indicated by Mössbauer studies[11–13] and the absence of clear multiplet splitting due to the Fe in x-ray photoelectron spectroscopy measurements on our samples suggest the iron is not the source of pair breaking. While an intrinsic pair breaking mechanism cannot be entirely ruled out at this time, it does seem highly unlikely.

This leaves (iv) which is essentially a two-band model in which one band remains normal. This is entirely consistent with our results, with γ_s representing the density of states of the normal band and γ_n the total density of states. In order for the normal band to remain stable against condensation of Cooper pairs it must have a net repulsive electron-electron interaction and be at most very weakly coupled with the superconducting band(s) (see, for example, Ref. 21). The topologically complex Fermi surfaces typical of 3d transition metals, and especially so for ternary materials, may well provide the necessary pockets of electrons to explain the anomalous superconducting properties of these materials. The dramatic pressure and alloying properties can be understood in this model as arising from the rapid changes which might be expected in these pockets of electrons, both in surface area of the pockets in momentum space and topology of the surface in general, with a pressurelike variable. Band-structure calculations would be very useful in this respect.

SUMMARY

Anomalous behavior is observed in the superconducting properties of $Lu_2Fe_3Si_5$, $Sc_2Fe_3Si_5$, and $Y_2Fe_3Si_5$. Low-temperature specific-heat measurements indicate a large linear term in the superconducting state and a reduced jump in the specific heat significantly less than the BCS value of 1.43, indicating normal electrons in the superconducting state. These properties can all be understood in terms of a topologically complex Fermi surface in which pockets of electrons remain in the normal state well below T_c.

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