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Vining, Cronin Beals

SUPERCONDUCTIVITY AND LONG RANGE MAGNETIC ORDER IN TERNARY RARE EARTH IRON SILICIDES

Iowa State University

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Superconductivity and long range magnetic order in ternary rare earth iron silicides

by

Cronin Beals Vining

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

> Department: Physics Major: Solid State Physics

Approved:

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DEDICATION

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to Beth

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Abstracts

- "Low Temperature Heat Capacity of Superconducting Ternary Iron Silicides," C. B. Vining and R. N. Shelton, Bulletin of the American Physical Society, <u>27</u>, (1982) 639.
- "Superconductivity in the Er-Fe-Si Ternary System," C. B. Vining and R. N. Shelton, Bulletin of the American Physical Society, <u>28</u>, (1983) 300.

Publications

- "Pressure Dependence of the Superconducting Transition Temperature of (Th_{1-X}Y_X)Rh₄B₄," C. B. Vining and R. N. Shelton, <u>Ternary Supercon-</u> <u>ductors</u>, p. 243, eds. G. K. Shenoy, B. D. Dunlap and F. Y. Fradin, North-Holland, New York (1981).
- "Lattice Instability (bcc-tetrag. Transition) and Superconductivity in La₃X₄ Base Materials (X = S, Se)," K. A. Gschneidner, Jr., K. Ikeda, Y. -C. S. Yeh, B. J. Beaudry, O. D. McMasters, C. B. Vining and R. N. Shelton, <u>IV International Conference on Superconductivity in d- and f-Band Metals</u>, p. 431, eds. W. Buckel and W. Weber, Karlsruhe, West Germany (1982).
- 3. "Low Temperature Heat Capacity of Superconducting Ternary Iron Silicides," C. B. Vining, R. N. Shelton, H. F. Braun, and M. Pelizzone, Phys. Rev. B<u>27</u>, 2800 (1983).

VITA

- "Low Temperature Heat Capacity of Antiferromagnetic Ternary Iron Silicides RE₂Fe₃Si₅," C. B. Vining and R. N. Shelton, submitted to Phys. Rev. B.
- 5. "Superconductivity and Long Range Magnetic Order in Ternary Rare-Earth Iron Silicides," C. B. Vining, doctoral thesis, (1983) unpublished.

Field of Study

Major Field: Physics

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Studies in Superconductivity and Magnetism

Under Dr. Robert N. Shelton

GENERAL INTRODUCTION

Since its discovery by Onnes $^{1-3}$ in 1911 and accelerated by the basic understanding provided by the theory of Bardeen, Cooper and Schrieffer 4 in 1957, superconductivity has provided the motivation for innumerable publications.⁵ Magnetic phenomena have been known since ancient times⁶ and advances in both fields have provided reasonably complete descriptions of the major features of superconducting materials as well as the large variety of magnetically ordered materials. Due to new discoveries, both subjects remain active areas of research. A notable example is the systematics of the occurrence of superconducting materials and the prediction of superconducting critical temperatures or at least an understanding of observed critical temperatures. At this time, it is still impossible to predict from first principles the superconducting critical temperature of a particular material or even to predict with certainty whether a specific material will or will not become superconducting. However, empirical rules exist for some classes of materials, such as the Matthias e/a rule⁷ which is fairly reliable in accounting for the superconducting transition temperatures in some systems of binary compounds.⁸

These fundamental questions, together with the potential technological applications in superconducting wires, magnets, generators and logic devices are strong motivating forces for finding superconducting materials with desirable or unusual physical and mechanical properties. While ternary materials which are superconductors have been known for some time,⁸ only in the last decade have intermetallic compouds of more than two elements been recognized for their potential to exhibit physical

properties unknown or very rare among the elements and binary compounds. The Chevrel phase materials $(\text{REMo}_6 S_8)^9$ and the rare-earth rhodium borides $(\text{RERh}_4 B_4)^{10}$ were the first examples of the "new" field of ternary superconductors. Because of their extraordinarily high upper critical fields (as high as 60 T),¹¹ the Chevrel phase compounds are already being considered as starting materials for the production of superconducting wires. Both classes of compounds exhibit coexistence of long-range antiferromagnetic order and superconductivity in some of their members¹²⁻¹⁵, which is entirely unknown among the elements or in binary compounds. ErRh₄B₄¹⁶ and HoMo₆S₈¹⁷ exhibit re-entrant superconductivity wherein the material becomes superconducting on cooling and then at a lower temperature re-enters a normal conducting and ferromagnetically ordered state.

In these two materials, there appears to be a narrow temperature region in which a complex oscillatory magnetic state, perhaps with nonzero magnetization, coexists with superconductivity.^{18,19} Considerable progress has been made in a theoretical understanding of these and other phenomena although many important questions remain unanswered.²⁰ The persistence of superconductivity in the presence of such large concentrations of magnetic ions is unknown among the elements or in binary compounds in which the superconducting transition temperature is ordinarily rapidly depressed by the introduction of even a few percent of magnetic material. z regular sublattice of magnetic ions present in some ternary compounds appears to be the major difference which allows these unique phenomena to occur. The depression of the superconducting transition temperature by paramagnetic impurities randomly distributed in a material is well

described by the theory of Abrikosov and Gorkov,²¹ and more recent theories which take various other effects into account.^{22,23} None of these theories, however, adequately describes the magnetic superconductors such as $ErRh_AB_A$.

These discoveries have led to great activity in the search for other ternary superconductors exhibiting similar properties. At present, there are over 25 such ternary systems, 24 , 25 which in most cases are largely unexplored. In many of these new materials, the magnetic behavior, while perhaps not so dramatic as the coexistence phenomena, is nevertheless very striking. HoRh₄B₄, unlike ErRh₄B₄, is not superconducting, but orders magnetically at 6.7 K in excellent agreement with mean field theory. ²⁶ The dependence of the magnetic ordering temperatures of the rhodium boride or Chevrel phase compounds on the rare-earth involved deviates strongly from that expected if the RKKY interaction were the dominant interaction. ²⁷ Neither of these features is at present fully understood. Ternary materials are providing new insights into the physics of superconductivity, long range magnetic order and the competition between these two collective phenomena.

While the two most extensively studied ternary systems (rare-earth rhodium borides and Chevrel phases) remain active subjects for investigation, several other new ternary systems exhibit unusual properties worthy of investigation. Several superconducting ternary systems involving 3-d elements have recently been reported. In particular, ternary compounds involving Fe and Co have been reported superconducting with transition temperatures as high as 6.1 K. Binary superconductors involving Fe or Co

Compound	Structure type	т _с (к)	Reference
CeCo ₂	Laves Phase	1.0	28
Hf ₂ Co	Ti ₂ Ni	0.56	8
La ₃ Co	Fe ₃ C	4.28	29
CoSi ₂	CaF ₂	1.22	30
Th ₇ Co ₃	Th ₇ Fe ₃	1.83	31
CoTi	W	0.71	8
Ti ₂ Co	Ti ₂ Ni	3.44	31
CoU	CoU	1.7	32
U ₆ Co	U ₆ Mn	2.3	32
CoZr ₂	CuA12	7.0	33
CoZr ₃	-	3.9	33
Y ₄ Co ₃	Ho ₄ Co ₃	2.5	38
Sc5 ^{Co4} Si10	Sc5Ir4Si10	4.9	34
Th ₇ Fe ₃	Th ₇ Fe ₃	1.86	31
U ₆ Fe	U ₆ Mn	3.9	32
Lu ₂ Fe ₃ Si ₅	Sc ₂ Fe ₃ Si ₅	6.1	35
Sc ₂ Fe ₃ Si ₅	Sc ₂ Fe ₃ Si ₅	4.5	35
Y ₂ Fe ₃ Si ₅	Sc ₂ Fe ₃ Si ₅	2.4	35
Tm ₂ Fe ₃ Si ₅	Sc ₂ Fe ₃ Si ₅	1.7	36
LaFe4P12	LaFe4P12	4.1	37

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Table 1. Selected superconducting phases with Fe or Co

are very rare; a search of the literature yields only those compounds listed in Table 1. Two ternary systems containing iron, $\text{RE}_2\text{Fe}_3\text{Si}_5^{35}$ and $\text{REFe}_4\text{P}_{12}$,³⁷ and one containing Co, $\text{RE}_5\text{Co}_4\text{Si}_{10}$,³⁴ have recently been reported. Fe and Co are ordinarily considered unlikely elements for superconductivity, and indeed are popular choices for studies of the effects of paramagnetic impurities on superconductivity. In these new systems, however, the 3-d elements seem to actually encourage the occurrence of superconductivity, often yielding superconducting transition temperatures higher than found in the analogous binary compounds (see Table 1). The compound $\text{Lu}_3\text{Ru}_3\text{Si}_5$, for example, exhibits no superconductivity above 1 K even though it is isostructural and isoelectronic with $\text{Lu}_2\text{Fe}_3\text{Si}_5$, which becomes superconductor³⁶ joining $\text{ErRh}_4\text{B}_4^{16}$ and $\text{HoMo}_6\text{S}_8^{17}$ and three ternary stannides^{40,41} as the six such compounds reported.

The systematics of the occurrence of superconductivity among the ternary compounds are, if anything, less clear than in the case of binary compounds. For some systems modifications of empirical rules successful for predicting trends among the binary compounds are moderately useful, but such rules are of very limited scope.¹³ If any trends are to be discerned, systematic and complete investigations of more of the ternary systems will be required. As the number of candidate systems grows larger, however, the choice of a model system becomes a growingly acute problem if the greatest benefit is to be gained from a given expenditure of effort. For the work presented in this dissertation, the system RE₂Fe₃Si₅ has been chosen for a number of reasons. We have attempted to address various questions re-

garding unusual physical properties of these materials such as the role of Fe in determining the superconducting properties, the nature of the reentrant superconductivity reported in $\text{Tm}_2\text{Fe}_3\text{Si}_5$, an understanding of the enormous effects of pressure and alloying on the superconducting transition temperatures, the systematics of the magnetic order and other questions. We have been more or less successful in these goals and have pursued various other questions which arose only as investigations continued, including anomalous critical behavior, strong crystalline electric field effects and indications of two band superconductivity.

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EXPERIMENTAL DETAILS

All samples used in this study were prepared by arc-melting mixtures of the elements in a Zr-gettered argon atmosphere. In most cases, the elements were mixed in stoichiometric amounts and weight losses were less than 0.5 percent, often much less. The sources and purities of the elements used are listed in the Appendix. Details of the sample preparation are given in each of the sections which follow. As standard procedure, powder X-ray diffraction data were taken using a Rigaku diffractometer and the ac susceptibility measured using a low frequency inductance technique from 1.2 to 20 K on each sample. In many cases, other measurements were performed the details of which are given in the sections which follow.

Calorimetry

All of the heat capacity measurements were performed on a heat pulsetype calorimeter constructed for this purpose. The cryostat is designed as an insert to existing helium dewar and gas handling systems. Several factors were considered in the design of this calorimeter. The following features were desired: 1) a working temperature range of 0.5 to 30 K; 2) insensitivity to mechanical vibrations; 3) long operation times (several hours to a few days); 4) economic use of liquid helium; 5) rapid realization of the lowest temperatures; and 6) simplicity of data collection.

To meet these requirements, a design used successfully at the University of California at San Diego,⁴² with some modifications, was decided upon. This design employs a modification of an adiabatic calorimeter. The lower portion of the calorimeter is indicated in Figure 1. The indium



- Flanges 1.
- Indium O-ring 2.
- 3. Vacuum can
- Vacuum can pumping line 4.
- 5.
- 6.
- 7. 8.
- 9.
- Vacuum can pumping line Coneva A. He³ condenser B. He⁴ evaporator He³ precooler (partially shown)/He³ return line He³ inlet He³ pot He³ pumping line He⁴ inlet (partially shown) 10. shown)
- 11.
- He pumping line Mechanical heat switch 12. actuator rod
- 13. Radiation shield support
- 14. Radiation shield
- Nylon addenda support 15.
- Gold plated heat switch 16.
- Gold plated addenda A. Upper half 17.

 - B. Lower half

Figure 1. Lower portion of heat capacity cryostat

O-ring seat arrangement shown here has been found to be very reliable. There are pumping lines for the vacuum can (not shown), the He³ system and the He⁴ system. The He⁴ system consists of the following: an opening in the flange to allow He⁴ from the bath surrounding the vacuum can to flow in through a 1/64" O.D. capillary to a chamber half-filled with sintered copper. A wire is inserted into the capillary to increase the flow impedance. Pumping on this chamber will cool the coneva (He³ condenser/ He⁴ evaporator) to about 1.2 K and maintain this temperature for an indefinite time period.

The first section of the He³ system is a 1/8" line for the supply of He³. This passes through a chamber on top of the flange, precooling the He³ to 4.2 K. From there, the He³ flows through a capillary to the condensing side of the coneva where the He³ condenses. The liquid He³ then flows through a 1/64" capillary to the He³ pot, a bellows which also supports the sample area. The central support of the calorimeter serves as the He³ pumping line. The back end of the He³ pump is then routed to the He³ return line.

The He³ pumping line serves as a heat switch. Once filled with He³ or He⁴, the interior of the vacuum can will cool, without the introduction of exchange gas into the sample area. The avoidance of helium adsorbed onto the sample is crucial to the determination of small heat capacities.

An additional mechanical heat switch to the sample holder itself is provided by a rod from the He^3 pot/bellows to the sample. The heat switch is actuated by a screw mechanism at room temperature on the top of the probe. The sample and addenda are supported by a thin-walled (0.005")

nylon support. This has several advantages over the more common nylon thread supports. The rigid support provides the sample with an environment which is insensitive to mechanical vibrations, important when dealing with samples of small heat capacities and temperatures below 1 K. The rigid support also allows a mechanical heat switch to come into direct contact with the addenda, with the consumate simplicity of heat switch design and ease of cooling the sample. The heat leak through the rigid support is still small enough to readily admit accuracies of better than 1 percent in the heat capacity.

Figure 2 shows the gas handling system. This arrangement provides great flexibility for the pumping of the various volumes available. The right half of the system is primarily intended for the pumping on the vacuum can itself. This system consists of a Sargent-Welch 1402 mechanical pump, a Varian HS-2 oil diffusion pump, supply lines for He, dry N_2 and air, and the associated pressure gauges. This system is capable of achieving a vacuum of 10^{-7} T. The left half of the gas handling system is a closed system intended for handling only He³. Valve 12 is normally kept closed, separating the two systems.

The He³ system consists of a Sargent-Welch 1402 mechanical pump, a Veeco EP 2A-1 oil diffusion pump, a cylinder of He³, a cold trap and the associated input and output ports. Normal operation of the He³ pot at low temperatures involves the following: the cold trap filled with liquid N₂, the diffusion pump warm and the mechanical pump running. Values 1, 3, 4, 6, 7, 8, 10, 11 would be open. Valves 2, 5 and 9 would be closed. It is important to note that the gas coming out the exhaust end of the 1402 pump is



Figure 2. Gas handling system

circulated back into the system. In this way, the system can operate indefinitely using small amounts of He³.

Figure 3 shows a block diagram of the electronics used with the calorimeter, consisting of two major sections: 1) a heater section, and 2) a thermometry section. The thermometry section consists of four thermometers, a selector, a commercial (SHE Corporation) potentiometric conductance bridge (PCB) and a strip chart recorder. Three of the four thermometers are germanium resistance thermometers (GRT) (S/N 6415, S/N 6273 and S/N 7704 from Cryo-Cal). The fourth thermometer is a Pt resistance thermometer. The GRTs have response times on the order of 3 msec and have very small heat capacities, making them appropriate for heat capacity measurements. The sample thermometer (S/N 6415) has varnished copper leads for good thermal contact to the sample/addenda. GRT S/N 6273 sits on the He³ pot which is in direct contact with the sample radiation shield. GRT S/N 7704 is attached to the coneva to help monitor this stage as is the Pt thermometer to aid in monitoring the initial cool down of the apparatus.

Each of these thermometers is connected to a selector box which selects the thermometer to be monitored by the PCB. The PCB uses a four probe low frequency (27.5 Hz) technique for measuring the conductance of the thermometers. An output of the PCB provides the difference between the actual conductance and a set conductance, determined by a ten turn potentiometer, which is then sent to the strip chart recorder. The PCB provides a simple, reliable and accurate method for measuring temperatures.



Figure 3. Heat capacity apparatus block diagram

The heater portion of the diagram consists of two heaters, a selector box, a current controller, two current sources, a digital timer and a digital voltmeter. The sample heater consists of about 30" of 0.001" diameter Pt-W wire, with a resistance of 1000 ohms at 300 K, wrapped onto the bottom half of the sample holder. The sample heater has two manganin current leads and two voltage leads, one connected at the sample, the other to the manganin current lead at the radiation shield, where all leads are thermally grounded. In this way, the heat developed in only one of the current leads is accounted for in determining the total power dissipated through the heater. Each current lead is about 4 ohms or 0.4% of the total heater resistance. This method approximately accounts for the heat generated in the current leads which is lost to the radiation shield. Using the lead compensation method, the accuracy of the power of the heat pulse should be better than 0.1%. The second heater is wrapped on the radiation shield support. This heater is used to provide temperature control of the radiation shield.

The selector box contains a 1000 ohm wire wound resistor in series with the sample heater. Measuring the voltage drop across this standard and the voltage drop across the heater yields, using Ohm's law, the power provided by the heater. The standard resistor also provides a means of monitoring the current through the auxiliary heater. The current controller (Figure 4) provides a reliable, bounceless switch for the current. The controller switches the current provided by the constant current source from a 1000 ohm dummy resistor to the heater and at the end of the pulse automatically back to the dummy load. This controller is essen-



Figure 4. Circuit diagram of heat capacity controller

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tially identical to that described by Goodrich.⁴³ The controller produces a nearly bounceless, reproducible pulse the duration of which is measured with the digital timer.

The constant current source (Figure 5) is a simple operational amplifier constant current supply, built with wire wound resistors for greater stability. The operational amplifier used is the OP-O7, a stable low current op amp from Precision Monolithics. This current source provides currents stable to 1 part in 10^6 for the duration of the heat pulse (2 sec to 5 min). A Keithley 192 programmable digital voltmeter is used for voltage measurements. The storage capability of this multimeter makes possible the measurement of both the standard resistor voltage (providing the current) and the heater voltage during a 2 second pulse.

The GRTs were calibrated in the range 0.9 to 30 K using the techniques, equipment and assistance of M. S. Anderson and C. A. Swenson.⁴⁴ The thermometers were first dipped into a liquid helium dewar 10 to 12 times and measured with the cryobridge discussed in reference 49 to check their reproducibility at 4.2 K. This relatively quick step can reveal unreliable thermometers before undertaking the entire calibration procedure. The thermometers discussed here all showed a high degree of reproducibility in these tests.

The thermometers were calibrated against a standard GRT noted for its reliability, longevity and accuracy. Forty-two data points were collected in the range 0.9 to 30 K. A least squares fit of these data to the form

$$\ln(T) = \sum_{i=1}^{N} A_i \ln(R)$$
(1)



Figure 5. Circuit diagram of constant current source

was made. This fitting procedure minimized the sum of

$$(T - T_{calc})^2 / T^2$$
 (2)

the absolute deviations in T. Seventh to ninth order fits covering three overlapping temperature ranges resulted in reasonable root mean square deviations (less than 0.5 mK) given by the standard form

$$(\sum_{j} (T_{j} - T_{calc})^{2})^{1/2}$$
 (4)

For GRT S/N 6415, the thermometer intended for use as the sample thermometer in the calorimeter, the coefficients of these fits, however, were found to be large and highly sensitive to small changes in the data. By scaling the data using the relation

$$\ln(R) = Ax + B \tag{5}$$

with A and B chosen such that $-1 \ll x \ll 1$, a much more satisfactory fit resulted. Fitting the full temperature range, 0.9 K to 30 K, to

$$ln(T) = \sum_{i=1}^{N} A_i X$$
 (6)

resulted in a RMSD = 0.25 mK for a polynomial of degree 13. Including more terms than this only marginally improved the fit, while a polynomial of degree 12 yielded a RMSD = 0.44 mK, significantly higher. Fitting the data without scaling the resistance values could not achieve as good a fit even with a much higher degree of fit. Moreover, using the scaling procedure, the coefficients are stable with respect to small changes in the data. Using the fits of the unscaled data required more than 10 digits of accuracy to achieve the desired accuracy in the calculated temperatures. Ten digits of accuracy were ample using the scaling technique, allowing the results of the fit to be used on a programmable calculator for use during heat capacity data collection.

Two thermometers required calibration below 1 K for use in the calorimeter. Thermometers S/N 6415 and S/N 6273 were chosen for this purpose since they are the most sensitive of the thermometers in the temperature range 0.3 to 1 K. The other thermometer's resistances rise too steeply in this region to be used accurately below 1 K. These thermometers were calibrated against a Cryocal GRT (S/N 17708) provided with calibration to 0.3 K. The two GRTs to be calibrated were mounted on the He^3 pot of the calorimeter with GE 7031 varnish in close proximity to each other. Conductance measurements were made using an SHE potentiometric conductance bridge (PCB). A data point consisted of an average of at least three measurements on each thermometer. A data point was not kept if the temperature varied by more than 1 mK during these measurements. Sixteen data points were collected in this manner in the region 0.35 to 1.4 K. These data were fit in a manner similar to that described above. yielding a RMSD = 0.25 mK. The two calibrations agree to 0.1% in the overlap region. These results have been incorporated into programs written for an HP-97 calculator, eliminating the need for referral to tables of temperatures and the interpolation that such tables require.

Sc₂Fe₃Si₅-TYPE CRYSTAL STRUCTURE

The Sc₂Fe₃Si₅-type crystal structure was first reported by Bodak et al.⁴⁵ and the range of formation of this structure type upon substitutions of other rare-earths for Sc and other transition metals for Fe has been studied by Segre³⁹ who reported 37 compounds with this structure type. The RE-Fe-Si equilibrium phase diagrams have been studied for RE = Sc,⁴⁶ Y and Gd⁴⁷ indicating 14, 7 and 8 ternary compounds, respectively, in these systems. Superconductivity has been reported for $Y_2Fe_3Si_5$, $Sc_2Fe_3Si_5$, $Lu_2Fe_3Si_5$, 35 Tm₂Fe₃Si₅, 36 and $Y_2Re_3Si_5$.³⁹ Sc₂Fe₃Si₅ crystallizes in a tetragonal unit cell with lattice parameters a = 10.225 Å and c = 5.275 Å and belongs to the space group P4/mnc. The crystallographic data for Sc₂Fe₃Si₅ as viewed along the c-axis. There are two crystallographically distinct Fe sites and three crystallographically distinct Si sites. The coordination numbers of Fe(1), Fe(2), and Sc are 13, 12 and 20, respectively.

The relatively high coordination numbers and low symmetry of the Fe and rare-earth sites play an important role in the physical properties of this class of compounds. The absence of clustering of transition metals which plays an important role in several other ternary superconducting systems is notable. The shortest Fe-Fe distances (2.67 Å) are still larger than Fe-Fe distances typical of Fe metal of Fe intermetallic compounds. The shortest Sc-Sc distances are 3.70 Å which, although shorter than the RE-RE distances found in either the rhodium borides (5.3 Å) or the Chevrel phase compounds (6.5 Å), are still larger than the RE-RE

Pearson symbol	tP40	
Space group	P4/mnc (No. 128)	
Lattice parameters (Å) ^a	a = 10.225(5) c = 5.275(5)	
X-ray density (g cm ⁻³)	4.79(1)	
Atomic parameters ^b		

Atom	Position	Point symmetry	x	У	Z
Sc	8(h)	m	0.0701	0.2500	0
Fe	8(h)	m	0.3790	0.3601	0
Fe	4(d)	222	0	1/2	1/4
Si	8(g)	2	0.1779	0.6779	1/4
Si	4(e)	4	0	0	0.2528
Si	8(h)	m	0.1799	0.4761	0

^aRef. 36. E.s.d. in parentheses. According to reference 45, a = 10.05 Å, c = 5.313 Å.

^bRef. 45. No E.s.d. were given.

distances found in the rare-earth metals (3.4 Å). The shortest Fe-Si (2.30 Å) and Sc-Si (2.57 Å) distances are shorter than the sums of the corresponding metallic radii (2.76 Å and 2.96 Å, respectively) indicating considerable covalent character to these bonds.⁴⁸ This may in part account for the nonmagnetic nature of the Fe atoms in these materials, which is discussed in detail below. Table 3 summarizes the crystal-lographic data for the eleven samples used in this study. The lattice



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Figure 6. Sc₂Fe₃Si₅-type crystal structure

	•	235		
Compound	a(A)	c(A)	c/a	V(A ³)
Sc ₂ Fe ₃ Si ₅	10.220(5)	5.273(3)	0.516	550.8
Y ₂ Fe ₃ Si ₅	10.43(1)	5.480(5)	0.525	596.1
Lu ₂ Fe ₃ Si ₃	10.352(5)	5.390(3)	0.521	577.6
Yb ₂ Fe ₃ Si ₅	10.36(1)	5.396(5)	0.521	579.2
Tm ₂ Fe ₃ Si ₅	10.371(7)	5.409(3)	0.522	581.8
Er ₂ Fe ₃ Si ₅	10.388(6)	5.427(4)	0.522	585.6
Ho2Fe3Si2	10.40(1)	5.446(6)	0.524	589.0
Dy ₂ Fe ₃ Si ₅	10.418(5)	5.461(4)	0.524	592.7
Tb ₂ Fe ₃ Si ₅	10.43(1)	5.483(5)	0.526	596.5
Gd ₂ Fe ₃ Si ₅	10.47(1)	5.521(5)	0.527	605.2
Sm ₂ Fe ₃ Si ₅	10.50(1)	5.562(5)	0.530	613.2

Table 3. Lattice parameters for $RE_2Fe_3Si_5^a$

^aEstimated standard deviation in parentheses.

parameters reported here are in excellent agreement with those reported by Braun,³⁵ but differ significantly with those reported by Bodak et al.⁴⁵
LOW TEMPERATURE HEAT CAPACITY OF SUPERCONDUCTING TERNARY IRON SILICIDES

I. INTRODUCTION

Ternary superconductors, particularly the Chevrel phase compounds and the rhodium borides, have been extensively studied in recent years.^{24,25} 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 (RE) 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 may be found among compounds containing 3d transition elements as intrinsic constituents.³⁴

Among binary iron compounds, only $U_6Fe (T_c = 3.9 \text{ K})^{32}$ and $Th_7Fe_3 (T_c = 1.86 \text{ K})^{31}$ are superconducting above 1 K. Recently, five ternary compounds containing iron as the transition metal $(RE_2Fe_3Si_5 \text{ with } RE = Lu,Sc,Y,Tm^{35,36,38}$ and $LaFe_4P_{12})^{37}$ have been reported superconducting. The ternary iron silicides, $RE_2Fe_3Si_5$, were first reported superconducting by Braun in 1980.³⁵ The properties of these materials are anomalous in several respects: (i) the effect of pressure on T_c is among the largest known $(dT_c/dp = -7 \times 10^{-5} \text{ K/bar for } Lu_2Fe_3Si_5 \text{ and } Sc_2Fe_3Si_5 \text{ and } dT_c/dp = 33 \times 10^{-5} \text{ K/bar for } Y_2Fe_3Si_5);^{49}$ (ii) the rapid depression of T_c with nonmagnetic impurities $(T_c \text{ drops below } 1 \text{ K for } 15\% \text{ Sc substituted for Lu in } Lu_2Fe_3Si_5);^{50}$ (iii) reentrant superconductivity has been reported in $Tm_2Fe_3Si_5;^{36}$ (iv) there is no magnetic moment on the iron in this structure as indicated by Mössbauer spectroscopy; 5^{1-53} and (v) a commensurate-

incommensurate magnetic transition has been observed in antiferromagnetic ${\rm Tb_2Fe_3Si_5}.$

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 $RE_2Fe_3Si_5$ materials (RE = Sm, Gd-Lu, Sc and Y). The low temperature heat capacity of the magnetic rare-earth compounds is discussed in the following chapter.⁵⁵

II. SAMPLE PREPARATION AND CHARACTERIZATION

Samples of $Lu_2Fe_3Si_5$, $Sc_2Fe_3Si_5$ and $Y_2Fe_3Si_5$ of 3-4 gm 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 5 days followed by 7 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 P4/mnc) with lattice parameters in agreement with those reported by Braun.³⁵ 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 microns with small amounts of impurities along the grain boundaries. Microprobe results indicate two major impurities of approximate compositions FeSi and REFe₃Si₇. Total impurities are estimated to be about 2% by volume in each sample.

Low frequency a.c. inductance measurements indicate superconducting transitions at 6.3 K, 4.4 K and 1.7 K for $Lu_2Fe_3Si_5$, $Sc_2Fe_3Si_5$, and $Y_2Fe_3Si_5$, respectively, in agreement with previous results.^{35,49} The transitions are sharp ($\Delta T_c = 0.2$ K) and consistent with bulk superconductivity.

Magnetic susceptibility measurements from 5 K 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 Figure 7.

In addition to the above samples, a series of five samples $Sc_2Fe_{3+\delta}Si_5$ (δ = -0.5, -0.1, 0.0, 0.1, 0.5) not used in the heat capacity measurements was 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 Sc₂Si₅, 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 5 samples are presented in Figure 8, 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, $\mathbf{T}_{\mathbf{C}}$ 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 ${\rm Lu_2Fe_3Si_5}$ and



Figure 7. Magnetic susceptibility for $Sc_2Fe_3Si_5$, $Y_2Fe_3Si_5$ and $Lu_2Fe_3Si_5$. [See text for details]



Figure 8. Superconducting transition temperatures (\bullet) of Sc₂Fe_{3+ δ}Si₅ compounds. [Error bars indicate width of the transition into the superconducting state; the transition temperature for the sample of Sc₂Fe₃Si₅ used in the heat capacity measurements is indicated at the right (\Box); the solid line is a guide for the eye]

 $Sc_2Fe_3Si_5$, and the extensive characterization of these samples play a major role in the discussion of the results below.

III. EXPERIMENTAL DETAILS

Low temperature heat capacity measurements were performed using a semi-adiabatic heat pulse-type calorimeter equipped with a mechanical heat switch, a circulating He^4 pot and a circulating He^3 pot. Mechanical noise introduced while operating the He^3 system prohibited accurate data acquisition below 1 K during the measurements, limiting the usable temperature range to 1.2 K - 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 ohm Pt-W heater wound on the sample holder. The duration of the heat 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.

The thermometry consists of a germanium resistance thermometer (GRT) and a commercially available potentiometric conductance bridge. The GRT was selected for its extended usable temperature range (0.3 K-30 K) and calibrated in this laboratory in the range 0.9 K-30 K against a GRT known for its stability and reliability as a secondary standard. The calibration procedure and equipment is described in Ref. 44. A second calibration,

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overlapping this one, was performed from 0.3 K-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 cooper. 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-K² and $\theta_D = 345$ K, in good agreement with the corresponding values for the copper reference equation.⁵⁶ Typically, the heat capacity of the addenda accounted for 35% to 55% of the total heat capacity measured in runs with Cu or the superconducting compounds discussed below.

IV. RESULTS

The low temperature heat capacities of $Lu_2Fe_3Si_5$, $Sc_2Fe_3Si_5$ and $Y_2Fe_3Si_5$ are shown in Figures 9, 10 and 11, respectively, where C/T is plotted against T^2 in the usual manner. A jump in the heat capacity at 6.3 K, 4.4 K and 1.7 K for Lu₂Fe₃Si₅, Sc₂Fe₃Si₅ and Y₂Fe₃Si₅, respectively, indicates the transition into the superconducting state. Deviations from linearity above T_c , especially in $Lu_2Fe_3Si_5$, are apparent. In each case, the data were fit in the temperature range from above $T_{\rm c}$ 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 4). 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 ${\rm T}^5$ term is quite large, contributing 13% of the total heat capacity at 10 K. The rapid variation of the lattice contribution and the higher ${\rm T}_{\rm C}$ (6.3 K) contribute somewhat smaller and larger, respectively, than the values resulting from the fit. No such discrepancy exists for Sc₂Fe₃Si₅, where the normal state data are more well behaved (i.e., the T⁵ contribution is smaller) and T_c is lower.

The jump in the specific heat at T_c is sharp for $Lu_2Fe_3Si_5$ ($\Delta T_c = 0.3 \text{ K}$) and $Sc_2Fe_3Si_5$ ($\Delta T_c = 0.35 \text{ K}$). The jump at T_c for $Y_2Fe_3Si_5$ is relatively broad ($\Delta T_c = 0.5 \text{ K}$) with significant contributions to C(T) from the superconducting state as high as 2 K. The somewhat lower value of T_c than previously reported³⁵ 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 , $\Delta C/\gamma_nT_c$, is significantly reduced from the BCS value of 1.43 (see



Figure 9. C/T vs. T^2 for Lu₂Fe₃Si₅. [The inset indicates the coefficient of the linear term in the the heat capacity of the normal state (γ_n) and the superconducting state (γ_s), in mJ/ Mole-K²]

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Figure 10. 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-K²]



Figure 11. 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-K²]

,,	Units	Lu ₂ Fe ₃ Si ₅	Sc ₂ Fe ₃ Si ₅	Y ₂ Fe ₃ Si ₅
T	ĸ	6.25±0.15	4.46±0.2	1.68±0.25
Υ _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	7.97x10 ⁻⁴	8.82x10 ⁻⁵	1.77x10 ⁻⁴
θD	К	485	561	490
∆C	mJ/Mole-K	173.0	80.3	25.4
ΔC/ _{Yn} 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)	sts./eV-atom-spin	0.59	0.47	0.41
λ		0.51	0.45	0.39
MW	gm/Mole	657.9	397.9	485.8

Table 4. Superconducting and normal properties of ternary iron silicides

Table 4), 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 formula⁵⁷ with $\mu^* = 0.1$ (Table 4) indicate these materials are intermediate coupled superconductors.

Below T_c, the heat capacity of $Lu_2Fe_3Si_5$ is remarkably simple (see insert Figure 9). From 2.4 K to 6 K, the data can be described by C = $\gamma_sT + \beta_sT^3 = 10.14 T + 1.346 T^3 mJ/Mole-K$ 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 Figure 10). Extrapolation of the lowest temperature data for $Sc_2Fe_3Si_5$ indicate $\gamma_s = 13.6 \text{ mJ/Mole-K}^2$ or 61% of the normal state gamma ($\gamma_n = 22.2 \text{ mJ/Mole-K}^2$). 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 $\gamma_s \neq 0$ in this case also.

V. DISCUSSION

The anomalously large T^5 contribution observed in the normal state heat capacities of these materials, especially in Lu₂Fe₃Si₅, 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^{58,59} 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) the 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 categories 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 a.c. inductance and heat capacity measurements indicates good sample homogeneity, ruling out (i) above.

Attributing ${\bf Y}_{\rm S}$ in ${\rm Lu}_2{\rm Fe}_3{\rm Si}_5$ to impurities of 5% of the material yields a $\gamma_{imp} = 0.31 \text{ mJ/g-K}^2$. This is much larger than the γ of any of the elements, except α -Mn (γ = 0.32 mJ/g-K²).⁶⁰ 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 pairbreaking are plausible in view of the large concentration of Fe present in these materials. However, the magnetic susceptibility measurements shown in Figure 7 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 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 5^{1-53} and the absence of clear multiplet splitting due to the Fe in XPS measurements on our samples suggests 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 electronelectron interaction and be at most very weakly coupled with the superconducting band(s) (see for example Ref. 61). The topologically complex Fermi surfaces typical of 3-d 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 pressure-like variable. Band structure calculations would be very useful in this respect.

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VI. 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 .

LOW TEMPERATURE HEAT CAPACITY OF ANTIFERROMAGNETIC TERNARY IRON SILICIDES

I. INTRODUCTION

Much attention has been focused on the competition between superconductivity and magnetism observed in several ternary rare earth compounds.¹² Even in the absence of superconductivity, however, a complete understanding of the nature of the magnetic order in many of these compounds is still lacking. Particular attention has been given to the anomalous magnetic ordering temperatures in the RERh₄B₄ compounds²⁷ and the striking mean field-like ferromagnetic transition observed in HoRh₄B₄.²⁶ The recent discovery of superconductivity and magnetism in the RE₂Fe₃Si₅³⁵ compounds presents another ternary system in which the superconducting and magnetic properties depend strongly on the choice of the rare earth.

Mössbauer studies on $\text{RE}_2\text{Fe}_3\text{Si}_5$ compounds utilizing the ^{57}Fe resonance $^{51-53}$ indicate the iron atoms carry no magnetic moment in either of the two crystallographically distinct Fe sites. Mössbauer measurements using the 161 Dy resonance in $\text{Dy}_2\text{Fe}_3\text{Si}_5^{52}$ indicate a magnetic moment at the Dy site $(7.0 \ \mu_b)$ which is significantly reduced from the free ion value $(10.6 \ \mu_b)$. Antiferromagnetic order, as determined by susceptibility measurements, has been observed for $\text{RE}_2\text{Fe}_3\text{Si}_5$ compounds with RE = Gd - Tm. 53 Observation of a commensurate-incommensurate antiferromagnetic transition by neutron diffraction in $\text{Tb}_2\text{Fe}_3\text{Si}_5^{36}$ provided motivation for our present study

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of the low temperature heat capacity of the $RE_2Fe_3Si_5(RE = Sc, Y, Sm, Gd-Lu)$ compounds as a means of better understanding the nature of the superconductivity and magnetic order in these materials. The low temperature heat capacity data of the magnetically ordered $RE_2Fe_3Si_5$ compounds (RE = Sm, Gd-Yb) are reported here as part of a systematic study of ternary rare earth iron silicides.

II. EXPERIMENTAL DETAILS

Samples of $RE_{2}Fe_{3}Si_{5}$ (RE = Sm, Gd-Tm) were prepared by arc-melting stoichiometric mixtures of the elements in a Zr-gettered high purity argon atmosphere followed by successive heat treatments at 1200°C, 1000°C and 800°C for two days each in quartz ampoules filled with an argon partial pressure of 150 Torr. Following this treatment, the sample of $Sm_2Fe_3Si_5$ showed physical deformation and assumed the shape of the quartz ampoule. This observation indicates the melting point of Sm₂Fe₃Si₅ is at or below 1200°C. No indication of melting was observed in any of the other samples following this heat treatment. The sample of Yb₂Fe₃Si₅ was prepared in a somewhat different manner due to the relatively low boiling point and high vapor pressure of Yb. A nearly single phase sample of Yb₂Fe₃Si₅ was produced by arc-melting a eutectic composition of iron and silicon (20.5 at.%Si) with an excess of Yb over that required for a stoichiometric sample. This procedure was followed by melting in an additional amount of Si to achieve the stoichiometric composition. A sample of this "as cast" form was chosen for use in the heat capacity measurements since the annealing process resulted in a significant loss of Yb.

Powder x-ray diffraction patterns indicate all samples are single phase with lattice parameters in good agreement with previous results.³⁵ Low frequency ac inductance measurements indicate antiferromagnetic ordering temperatures also in good agreement with previous results.⁵² Details of the low temperature heat capacity measurement technique are discussed above.

III. RESULTS

We first discuss our results for the low temperature heat capacity of each of the eight compounds $RE_2Fe_3Si_5(RE = Sm, Gd-Yb)$ on an individual basis and then point out trends observed throughout the series. In each case, the total heat capacity, after correcting for the addenda in the usual way,⁶² is expressed as

$$C = C_n + C_m + C_\rho + C_\rho$$
(7)

where C_n is the nuclear contribution arising from the interaction of the nucleus with the effective magnetic field at the nucleus, C_m is the magnetic contribution arising from the electrons in the unfilled 4f-shell of the rare-earth ions (assuming no direct contribution from the iron ions), C_e is the usual electronic contribution and C_g is the lattice contribution.

For each sample in this study, the electronic and lattice contributions to the heat capacity are assumed to be identical to that found in $Lu_2Fe_3Si_5$.⁶² A parameterization of the normal state heat capacity of $Lu_2Fe_3Si_5$ has, therefore, been subtracted from the heat capacity of each sample reported here. Thus, in the following discussion, unless otherwise specified, the heat capacity referred to is given by

 $C = C - C_e(Lu) - C_{\ell}(Lu) = C_n + C_m$ (8) where (Lu) refers to the appropriate values for $Lu_2Fe_3Si_5$. This assumption appears reasonable for all eight samples considered.

Several of these materials exhibit a relatively large nuclear Schottky anomaly. The contribution to the heat capacity from a nuclear Schottky anomaly at temperatures well above the maximum in the anomaly is expected to behave like

$$C_{n}/R = C_{2}/T^{2}$$
 (9)

where $\rm C_2$ is related to the effective magnetic field at the nucleus, $\rm H_{eff},$ by

$$C_{2} = 1/3(\mu H_{eff}/kI)^{2}I(I + 1)$$
(10)

where μ is the effective magnetic moment of the nucleus, k is Boltzmann's constant and I is the nuclear spin. 63

The magnetic contribution to the heat capacity near the critical temperature is expected to behave like

$$C_{m} = A[1 - T/T_{M}]^{-\alpha}$$
 (11)

where α is a small positive number. In the limiting case of $\alpha \rightarrow 0$, the alternate form

$$C_{m} = A \ln|1 - T/T_{M}|$$
 (12)

may be more applicable.⁶⁴ Well below the magnetic ordering temperature, the magnetic heat capacity can often be characterized by simple power laws or exponentials. An isotropic 3-dimensional antiferromagnet, for example, is expected to have a spin wave contribution to the heat capacity proportional to T^{3} .⁶³ The applicability of these various forms to our experimental results will be discussed in Section IV-F.

Each of the Figures 12 through 19 presents the low temperature heat capacity of one of the eight samples discussed above. In each case, the heat capacity obtained in the manner discussed above is plotted in units of R (8.314 J), the molar gas constant, per mole of rare earth. Thus, one mole of $Sm_2Fe_3Si_5$ contains two moles of the rare earth, Sm in this case. In each case, the entropy obtained by numerically integrating the heat capacity

$$S = \int C/T \, dT \tag{13}$$

is also plotted in the same units. The lower limit of the integration is taken as the lowest temperature obtained rather than zero Kelvin, but in most cases the error introduced by this procedure is less than one percent.

The low temperature heat capacity and entropy of $Sm_2Fe_3Si_5$ from 0.5 K to 30 K are presented in Figure 12. The four distinct maxima at 5.05 K, 6.19 K, 7.35 K and 8.96 K indicate four magnetic phase transitions. This is in contrast to the complete absence of features in the susceptibility as determined by low frequency ac inductance techniques both on this sample and on a sample studied previously.³⁹ The absence of any large change in susceptibility, together with the features evident in the heat capacity indicate the ordering at each of the peaks in the heat capacity is antiferromagnetic as reported previously for most of the other $RE_2Fe_3Si_5$ compounds.⁵² Furthermore, the entropy shows a distinct plateau well above all the transitions at $\Delta S = 0.62$ R, ~ R ln(2), indicating the electronic ground state in this compound is a doublet.

The inset of Figure 12 indicates an increase in the heat capacity below 1 K, apparently due to the high temperature side of a nuclear Schottky anomaly which should behave like Eq. (9) well above the maximum in the Schottky anomaly. From a graph of ΔC vs. $1/T^2$, C_2 is estimated to be 0.014 R K². Using the above value of C_2 , I = 7/2, μ = 0.4 μ_N and Eq. (10), an effective field of 12 megagauss at the Sm nucleus is calculated. An effective field typical of Sm metal derived in a similar manner is 3.3



Figure 12. The magnetic contribution to the heat capacity and entropy for Sm₂Fe₃Si₅. [The inset indicates the nuclear Schottky anomaly expected for Sm metal (solid line) and the observed heat capacity for Sm₂Fe₃Si₅ below 2 K]

megagauss,⁶³ much lower than the value for this ternary silicide. Indeed, a nuclear anomaly typical of Sm metal, indicated by the solid line in the inset to Figure 12, should be quite small and nearly unobservable at the lowest temperatures reached in this experiment. The possible origin of such a large effective field is considered in Section IV-E.

The low temperature heat capacity and entropy of $Gd_2Fe_3Si_5$ are presented in Figure 13. A single prominent peak is evident in the heat capacity at 8.40 K. As expected, there is no indication of a nuclear anomaly for Gd. There is, however, an inflection in the heat capacity below the antiferromagnetic ordering temperature. A plateau from about 2.5 K to 6.5 K in a plot of $\Delta C/RT$ against temperature shown in the inset in Figure 13 indicates the heat capacity has a large linear term in this temperature range. The possible origin of such a large linear term and its relation to spin waves will be discussed in Section IV-F.

As expected for Gd, which is an S-state ion and, therefore, unaffected by crystalline electric fields (CEF), the entropy associated with the full Hund's rules J, i.e., R $\ln(2J + 1) = R \ln(8) = 2.08$ R, is observed. The entropy at 28 K is $\Delta S = 2.02$ R in excellent agreement with the total entropy expected.

The low temperature heat capacity and entropy of $Tb_2Fe_3Si_5$ are presented in Figure 14. Two large peaks are observed in the heat capacity at



Figure 13. The magnetic contribution to the heat capacity and entropy for $Gd_2Fe_3Si_5$. [The inset indicates a large linear contribution to the heat capacity of $Gd_2Fe_3Si_5$ between 2 K and 6 K]



Figure 14. The magnetic contribution to the heat capacity and entropy for $\mathsf{Tb}_2\mathsf{Fe}_3\mathsf{Si}_5$

10.02 K and 7.06 K in excellent agreement with previous susceptibility and neutron diffraction results.^{52,54} Neutron diffraction results indicate a transition at 10 K to an antiferromagnetically ordered state in which the magnetic structure is incommensurate with the lattice. This state is followed by a second transition at 7 K to a different antiferromagnetically ordered state which is commensurate with the lattice.⁵⁴ At the lowest temperatures attained, a slight upturn in the heat capacity with decreasing temperature reveals the presence of a nuclear schottky anomaly expected for Tb. While lower temperatures would be needed for a quantitative comparison, the magnitude of this anomaly is in qualitative agreement with that expected for Tb metal.

D. Dy₂Fe₃Si₅

The low temperature heat capacity and entropy of $Dy_2Fe_3Si_5$ are presented in Figure 15. One large peak is evident at 4.20 K indicating the onset of antiferromagnetic order consistent with previous susceptibility results. This peak is much steeper on the high temperature side than on the low temperature side of the maximum. This asymmetry will be discussed in detail in Section IV-D. Above the ordering temperature, the heat capacity remains near 0.4 R per mole RE atoms, exhibiting a broad maximum near 9 K. This is presumably attributable to an electronic Schottky anomaly brought about by the usual CEF effects.



Figure 15. The magnetic contribution to the heat capacity and entropy for ${\rm Dy}_2{\rm Fe}_3{\rm Si}_5$

The low temperature heat capacity and entropy of $Ho_2Fe_3Si_5$ are presented in Figure 16. The heat capacity of this sample is remarkably similar in many respects to the heat capacity of $Dy_2Fe_3Si_5$. One large peak is evident in the heat capacity at 2.82 K, indicating the onset of antiferromagnetic order consistent with previous susceptibility results. The peak at 2.82 K is quite asymmetric and, as for $Dy_{2}Fe_{3}Si_{5}$, much steeper on the high temperature side than on the low temperature side. Above the ordering temperature, the heat capacity remains large (~0.6 R) and increases slowly with temperature to 28 K. Below 2 K, the heat capacity increases with decreasing temperature as expected qualitatively for the nuclear Schottky anomaly associated with the Ho nucleus. The inset to Figure 16 shows the data at temperatures below the minimum in the heat capacity (T < 1.9 K). From this plot, an estimate of the coefficient C_2 in Eq. (9) may be made for the nuclear Schottky contribution. Specifically, if the magnetic contribution goes like T³ as expected for an isotropic 3-dimensional antiferromagnetic spin wave, then the intercept in the inset of Figure 16 will represent the coefficient C_2 in the nuclear contribution to the heat capacity. The value for C $_2$ resulting from this is C $_2$ = 0.18 R. Using I = 7/2, μ = 4.08 μ_N and Eq. (10), the effective field at the Ho nucleus is estimated to be 4.3 megagauss, compared to an effective field of 7.5 megagauss calculated in a similar manner for Ho metal.63

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Figure 16. The magnetic contribution to the heat capacity and entropy for Ho₂Fe₃Si₅. [The inset indicates the nuclear Schottky anomaly below 1.8 K (see Sections III-E and IV-E for details)]

The low temperature heat capacity and entropy of $Er_2Fe_3Si_5$ are presented in Figure 17. Large peaks are evident in the heat capacity at 2.35 K and 2.78 K in this figure. The data between 2.2 K and 3.0 K are presented in the inset to Figure 17 on an expanded temperature scale and a compressed heat capacity scale as compared with Figures 12 through 19. The feature marked T_{M1} in the inset at 2.78 K is the smaller of the two peaks evident in the main figure. The magnitude of the feature at 2.35 K is more than a factor of 2 larger than any of the other features observed in this system of compounds. This feature is extremely sharp in temperature with a total width of less than 75 mK. There are two clear peaks in this feature at 2.352 K (T_{M4}) and 2.381 K (T_{M3}). A shoulder at 2.401 K defined by only two points is also indicated by T_{M2} in the inset. These data were taken in four successive runs and in two different experiments, eight weeks apart. The excellent agreement attests to the reproducibility of these magnetic phenomena. The average interval between data points in the region of the features at 2.3-2.4 K is less than 3 mK. Finer resolution might resolve more clearly the peak at T_{M2} . Note that the heat capacity in the region from 2.2 K to 2.35 K which appears essentially constant in the inset to Figure 17 is in reality a rapidly increasing function of temperature as can be seen by comparison to the main figure. The sharp rise in the heat capacity on the low temperature side of T_{M4} can be identified in the main figure by the sudden change in the density of data points near



Figure 17. The magnetic contribution to the heat capacity and entropy for Er₂Fe₃Si₅. [The inset indicates the magnetic contribution to the heat capacity for Er₂Fe₃Si₅ between 2.2 K and 3.0 K; note the change of scale]

2.3 K. The data rapidly rise from near 1.1 R just below T_{M4} to well off the scale of the main figure.

The heat capacity above the ordering temperatures drops to 0.15 R near 4.5 K and then rises for temperatures above this point. This rise is attributed to an electronic Schottky anomaly brought about by CEF effects. At the very lowest temperatures, the heat capacity begins to rise with decreasing temperatures, indicating a nuclear Schottky anomaly. Lower temperatures would be required for a quantitative estimate of the temperature dependence of this anomaly; however, the size of the feature is in qualitative agreement with the anomaly observed in Er metal.

G. Tm₂Fe₃Si₅

The low temperature heat capacity and entropy for $Tm_2Fe_3Si_5$ are presented in Figure 18. A large peak in the heat capacity is evident at 1.06 K indicating the onset of antiferromagnetic order. The heat capacity decreases above 1.06 K with increasing temperature until 7 K, after which it again increases. This increase in heat capacity above 7 K is attributed to CEF effects. The entropy shows a plateau at about 0.69 R \approx R ln(2) from 2 K to 10 K reflecting the small heat capacity in this region. The value of the entropy in the plateau indicates the magnetic ground state in $Tm_2Fe_3Si_5$ is a doublet. Attempts to fit the low temperature side of the peak in the heat capacity to a logarithmic divergence as given by Eq. (12) resulted in an unreasonably large value for T_M suggesting that the heat capacity may be finite at the antiferromagnetic ordering temperature. Possible reasons for this will be discussed in Section IV-D.


Figure 18. The magnetic contribution to the heat capacity and entropy for ${\rm Tm}_2{\rm Fe}_3{\rm Si}_5$

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The low temperature heat capacity and entropy for $Yb_2Fe_3Si_5$ are presented in Figure 19. A peak in the heat capacity at 1.70 K indicates the onset of antiferromagnetic order. The heat capacity decreases with increasing temperature above the ordering temperature of 1.70 K until 10 K where the heat capacity begins to increase with increasing temperature. The increase at higher temperatures is attributed to an electronic Schottky anomaly due to the CEF splitting of the 4f-shell of Yb. The appearance of magnetic order indicates that Yb is in a trivalent state in this compound rather than the more common, nonmagnetic divalent state. The trivalent state for Yb is also indicated by the lattice parameters for Yb₂Fe₃Si₅ when compared to other members of the RE₂Fe₃Si₅ series.³⁵

A relatively flat region in the entropy from 8 K to 15 K near the value 0.68 R \approx R ln(2) indicates the magnetic ground state in Yb₂Fe₃Si₅ is a doublet. The heat capacity above the magnetic ordering temperature exhibits negative curvature from 1.7 K to about 3 K and the general shape is suggestive of a Schottky anomaly. Indeed, the entropy at the transition is only 0.2 R, much lower than that expected for a doublet, the simplest degenerate ground state. This suggests that the magnetic ground state consists of two closely spaced singlets, with the next excited state at a considerably higher temperature.



Figure 19. The magnetic contribution to the heat capacity and entropy for $Yb_2Fe_3Si_5$

IV. DISCUSSION

A. Ordering Temperatures

Having briefly discussed the low temperature heat capacity of each of the members of the series $RE_2Fe_3Si_5$, we now turn our attention to some of the systematic trends observed in these data. Figure 20 and Table 5 present the ordering temperatures for each of the $RE_{2}Fe_{3}Si_{5}$ compounds (RE = Sm - Yb, except Eu which does not form a ternary compound in this structure). More than one transition temperature is indicated for Sm₂Fe₃Si₅, $Tb_2Fe_3Si_5$ and $Er_2Fe_3Si_5$ as discussed in Sections III-A, C and F. The lower transition for Er₂Fe₃Si₅ indicated in Figure 20 actually represents the closely spaced group T_{M2} , T_{M3} and T_{M4} as desginated in Figure 17. The magnetic ordering temperatures for a series of isostructural and isoelectronic metals where the indirect RKKY exchange interaction is the main interaction between the magnetic moments are expected to scale as S(S + 1)where S is the spin of the local moment or in the case where L, the orbital angular momentum, is not quenched as $(g_{J} - 1)^{2}J(J + 1)$ where g_{J} is the Lande g factor and J is the total angular momentum of the local moment. The latter case is more usual for the rare-earth elements.

The solid line in Figure 20 represents the ordering temperatures expected for the series $RE_2Fe_3Si_5$ normalized to the observed ordering temperature in $Gd_2Fe_3Si_5$ for the case where S is a good quantum number. The dashed line is similarly normalized to the observed ordering temperature of $Gd_2Fe_3Si_5$ and gives the expected ordering temperatures for the case where J is a good quantum number. Considering only those compounds for



Figure 20. Magnetic ordering temperatures for $RE_2Fe_3Si_5$ compounds. [The solid line indicates ordering temperatures expected if the effective moment on the RE varies as S and the dashed line indicates the ordering temperatures expected if the effective moment varies as J]

Compound	τ _Μ (κ)	s(T _M)/R	J	ln(2J+1)	S(28 K)/R
Yb ₂ Fe ₃ Si ₅	1.70	0.20	7/2	2.08	0.77 ^a
Tm ₂ Fe ₃ Si ₅	1.06	0.35	6	2.56	0.938
Er ₂ Fe ₃ Si ₅	2.79	0.50	15/2	2.77	1.55
	2.401	0.325			
	2.381	0.286			
	2.352	0.237			
Ho ₂ Fe ₃ Si ₅	2.82	0.44 ^b	8	2.83	2.03
Dy ₂ Fe ₃ Si ₅	4.20	0.50	15/2	2.77	1.40
Tb ₂ Fe ₃ Si ₅	10.02	0.51	6	2.56	1.03
	7.06	0.15			
Gd ₂ Fe ₃ Si ₅	8.40	1.42	7/2	2.08	2.02
Sm ₂ Fe ₃ Si ₅	8.96	0.49	5/2	1.79	1.29
	7.35	0.38			
	6.19	0.26			
	5.05	0.14			

Table 5. Magnetic properties of rare-earth ternary iron silicides

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Note: Entropy is in units of R per mole of rare earth.

^aAfter correcting for Yb weight loss (see Section II).

^bAfter correcting for the nuclear contribution (see Section IV-E).

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which one ordering temperature is observed, $Gd_2Fe_3Si_5$, $Dy_2Fe_3Si_5$, $Ho_2Fe_3Si_5$, $Tm_2Fe_3Si_5$ and $Yb_2Fe_3Si_5$, either of the two curves gives reasonable agreement between the expected and observed magnetic ordering temperatures. Of this group, only $Yb_2Fe_3Si_5$ lies far from the theoretical curves. This may be related either to the significant splitting of the ground state doublet in this compound or to mixed valence effects, often observed in Yb compounds.

Those compounds exhibiting multiple transitions, $Sm_2Fe_3Si_5$, $Tb_2Fe_3Si_5$ and $Er_2Fe_3Si_5$, have transition temperatures falling considerably above either of these curves. In each case, however, the lowest transition is reasonably close to the S(S + 1) curve. The rough agreement between the ordering temperatures and the trend predicted by the S(S + 1) curve or the $(g_J - 1)^2J(J + 1)$ (the de Gennes factor) curve, particularly for the heavy rare earth compounds (RE = Gd - Tm), indicates the major mechanism responsible for the magnetic ordering in these compounds is the usual RKKY indirect exchange interaction. In particular, there is no evidence in our data to indicate dipole-dipole interactions are important, as has been suggested for these compounds.⁵² Furthermore, the full moment or some effective moment which varies nearly as J (or perhaps S) determines the ordering temperatures in these compounds.

B. Coupling Constants

In mean field theory, the inter-RE coupling constant J' is related to the magnetic ordering temperature by

 $T_{M} = 2J^{T}S(S + 1)z/3k$ (14)

when S is a good quantum number and by

$$T_{M} = J'(g_{1} - 1)^{2} J(J + 1) z/3k$$
(15)

when J is a good quantum number where z is the number of nearest neighbor RE atoms.²⁷ Strictly speaking, there are only two nearest neighbor RE atoms in this structure due to the low symmetry of the RE site; however, two additional RE atoms are positioned at RE-RE distances only about 1% greater than for the two nearest neighbors. Therefore, using z = 4, to account for these four "nearest neighbor" RE atoms, the ordering temperature of $Gd_2Fe_3Si_5$ ($T_M = 8.40$ K), J = 7/2 and $g_J = 2$ yields $J' = 1.7 \times 10^{-5}$ eV.

The depression of the superconducting transition temperature of $Lu_2Fe_3Si_5$ by Gd impurities in $(Lu_{1-x}Gd_x)_2Fe_3Si_5$ can be used to estimate J, the conduction electron-RE exchange coupling constant. In the theory of Abrikosov and Gorkov, the depression of the superconducting transition temperature is related to the concentration of magnetic impurities in the limit of low impurity concentration by

$$dT_{c}/dn = 5dT_{c}/dx$$

$$= -\frac{\pi^{2}N(0)}{2k} J^{2}(g_{J} - 1)^{2}J(J + 1)$$
(16)

where dT_c/dn is the rate of depression of T_c per atomic percent impurity, dT_c/dx is the rate of depression of T_c per atomic fraction of Gd in Lu and N(0) is the density of states at the Fermi level.²⁷ Using $(dT_c/dx)/((g_j - 1)^2 J(J + 1)) = 4.9$ K per at. fraction Gd from Ref. 39 and N(0) = 0.59 sts./eV-atom-spin from Ref. 62, J is estimated to be 2.7×10^{-2} eV. To order of magnitude J and J' are related by²⁷

$$J = (J'N(0))^{1/2}$$
(17)

Using J' derived above from the ordering temperature of $Gd_2Fe_3Si_5$ yields $J = 5.4 \times 10^{-3}$ eV. This is in reasonable agreement with the estimate from the superconducting data, especially considering the crude nature of these estimates. Both estimates suggest the conduction electron-RE coupling is strong enough to mediate the indirect exchange interaction as has been previously reported for the RERh₄B₄ compounds.²⁷

C. CEF Effects

Figure 21 presents the entropy observed at the highest magnetic transition (when there is more than one transition temperature) for each of the eight compound discussed in Section III as well as the entropy at 28 K for each compound. The dashed line represents the entropy available for each compound assuming a total angular momentum J given by Hund's rules. The entropy associated with the nuclear Schottky anomaly in $Ho_2Fe_3Si_5$ has been neglected for the purposes of this figure. Only $Gd_2Fe_3Si_5$ exhibits nearly the full entropy at 28 K available from the total quantum number J = 7/2. This is expected for Gd compounds, since L = 0 in this case and CEF effects are, therefore, absent to first order. Considerably higher temperatures than attained in these experiments would be needed to observe all the entropy available from the full, Hund's value of J in each of the other compounds. This indicates that CEF effects are indeed quite important in these compounds, in agreement with previous susceptibility and Mössbauer results.^{52,53} For the compounds with non-S state rare-earth elements (i.e., excluding $Gd_2Fe_3Si_5$), the entropy at 28 K





peaks at $Ho_2Fe_3Si_5$ with J = 8, the largest value of the total angular momentum.

In five of these compounds, $Sm_2Fe_3Si_5$, $Tb_2Fe_3Si_5$, $Dy_2Fe_3Si_5$, $Ho_2Fe_3Si_5$ and $Er_2Fe_3Si_5$, the entropy at the transition is very nearly 0.5 R (see Figure 21). This is especially surprising since the number of transitions observed varies from one transition $(Dy_2Fe_3Si_5)$ to four transitions $(Sm_2Fe_3Si_5)$. The amount of entropy below the transition is very nearly the value predicted by a 3-dimensional Ising model (0.511 R) for a spin 1/2 systems on a diamond lattice (z = 4).⁶⁴ This indicates that in each of these five compounds, the magnetic ground state is a doublet as compared to the considerably higher degeneracy expected from Hund's rules. The doublet ground state is directly observed in $Sm_2Fe_3Si_5$ where the entropy indicates (Figure 12) that the next excited state is considerably higher than the ordering temperature.

In $\text{Tm}_2\text{Fe}_3\text{Si}_5$ (Figure 18) and $\text{Yb}_2\text{Fe}_3\text{Si}_5$ (Figure 19), the entropy also indicates that the ground state is a doublet, as previously discussed. In both cases, the entropy below the ordering temperature is well below 0.5 R indicating a large fraction of the R ln(2) of entropy is contained in the high temperature tail occurring above the ordering temperature. This suggests that the doublet is not entirely degenerate. Indeed, the heat capacity above the ordering temperature in $\text{Yb}_2\text{Fe}_3\text{Si}_5$ appears similar to that expected from a two level Schottky anomaly. This implies the CEF effects are large enough to split the doublets, presumably via the spin orbit coupling.

D. Critical Behavior

As discussed in Section III, the peak in the heat capacity of several of these compounds is very asymmetric, appearing steeper on the high temperature side than on the low temperature side. Figure 22 presents the heat capacity near the magnetic ordering temperatures for three of these samples, $Dy_2Fe_3Si_5$, $Ho_2Fe_3Si_5$ and $Er_2Fe_3Si_5$, both above and below the ordering temperatures. In the case of $Er_2Fe_3Si_5$, only the highest ordering temperature (T_{M1}) is considered. A logarithmic divergence such as described by Eq. (12) will appear as a straight line on such a plot and of the six lines in this figure, only four are straight. Below the critical temperature, the data for $Dy_2Fe_3Si_5$ and $Ho_2Fe_3Si_5$ (solid circle and solid triangle, respectively, in Figure 22) appear as straight lines and are nearly parallel to each other. The data for $Er_2Fe_3Si_5$ also appear to diverge logarithmically below T_{M1} as evidenced by the solid squares in Figure 22.

Above the critical temperatures, the situation is very different. The data for $\text{Er}_2\text{Fe}_3\text{Si}_5$ appear logarithmic as evidenced by the open squares in Figure 22; however, there is pronounced curvature in the data above the critical temperatures for both $\text{Dy}_2\text{Fe}_3\text{Si}_5$ and $\text{Ho}_2\text{Fe}_3\text{Si}_5$. Above the critical temperatures, the data for $\text{Dy}_2\text{Fe}_3\text{Si}_5$ and $\text{Ho}_2\text{Fe}_3\text{Si}_5$ appear to diverge with a critical exponent of 1, that is

 $C = A(T/T_M - 1)^{-1} + B = AT_M/(T - T_M) + B$ (18) as indicated in Figure 23 where we plot heat capacity versus $T_M/(T - T_M)$. The same critical temperatures are used in this figure as are used in Figure 22. Again, the curves for $Dy_3Fe_3Si_5$ and $Ho_2Fe_3Si_5$ appear very



Figure 22. The magnetic contribution to the heat capacity vs. |T/TM - 1| above (open symbols) and below (closed symbols) the magnetic ordering temperature for Dy₂Fe₃Si₅, Ho₂Fe₃Si₅ and Er₂Fe₃Si₅. [For Er₂Fe₃Si₅, TM refers to T_{M1} from Figure 6; note the logarithmic temperature scale]



 $T_{M}/(T-T_{M})$ Figure 23. The magnetic contribution to the heat capacity vs. $T_{M}/(T - T_{M})$ above the magnetic ordering temperature for $Dy_2Fe_3Si_5$, $Ho_2Fe_3Si_5$ and $Er_2Fe_4Si_5$

similar to each other and qualitatively different from the curve for $Er_2Fe_3Si_5$. These two plots clearly indicate that the highest transition in $Er_2Fe_3Si_5$ is typical of second order phase transitions, showing a nearly logarithmic divergence both above and below T_{M1} , while $Dy_2Fe_3Si_5$ and $Ho_2Fe_3Si_5$ show qualitatively different critical behavior and perhaps exhibit different critical exponents above and below their critical temperatures.

As discussed in Sections III-G and III-H, respectively, neither $Tm_2Fe_3Si_5$ nor $Yb_2Fe_3Si_5$ exhibits a clear logarithmic or even nearly logarithmic divergence either above or below its critical temperature, but rather suggests a finite maximum in the specific heat instead of a divergence. In the case of $Gd_2Fe_3Si_5$ and $Tb_2Fe_3Si_5$, the critical behavior is less clear due to a lower density of data points in this temperature range. $Sm_2Fe_3Si_5$ exhibits no sharp peaks in the heat capacity, but only more broadened maxima, especially when compared to the other seven compounds considered in this study. This may indicate sample inhomogeneities related to the lower melting point of this compound and the heat treatment of this sample. Inhomogeneities may also play a role in the critical behavior of $Yb_2Fe_3Si_5$ which was not annealed due to the low melting point of Yb.

The lower transitions in $\text{Er}_2\text{Fe}_3\text{Si}_5$, T_{M2} , T_{M3} and T_{M4} would appear to be of first order as indicated both by the huge magnitude of these heat capacity spikes and the sharp onset and completion of the transitions. Very sharp features are also observed near 2.35 K in low frequency inductance and resistivity measurements performed on this compound. Similarly, the lower transition in $\text{Tb}_2\text{Fe}_3\text{Si}_5$ is quite sharp and although the resolution of the heat capacity data is not as good for this compound, this may also be a first order transition.

E. Nuclear Schottky Anomalies

Several of these compounds exhibit a detectable nuclear Schottky anomaly at the lowest temperatures reached. In two cases, the anomaly is of sufficient magnitude to permit a quantitative estimate of the coefficient of the 1/T² term. As discussed in Sections III-E and III-A, respectively, the nuclear Schottky anomaly in ${\rm Ho_2Fe_3Si_5}$ appears to be only half as large as expected; whereas, the anomaly in $Sm_2Fe_3Si_5$ appears to be an order of magnitude larger than expected from the respective rare-earth metals. This may be related to the CEF effects which can alter the effective moment of the rare earth and, therefore, the effective magnetic field experienced by the nucleus. The large nuclear anomaly observed in $Sm_2Fe_3Si_5$, however, is especially difficult to understand. In the rareearth metals, the principal source of the effective field experienced by the nucleus is the orbital angular momentum, L.⁶³ CEF effects are expected to have their principal effect on L, thus reducing the field experienced by the nucleus and thereby reducing the observed nuclear Schottky anomaly. The dramatic increase in the nuclear anomaly in $Sm_2Fe_3Si_5$ is, therefore, difficult to understand since CEF effects can be expected only to reduce the effective field at the nucleus.

F. Spin Waves

The heat capacities of all eight compounds were examined graphically and numerically for indications of simple temperature dependences below the ordering temperatures. Functional forms such as simple power laws, exponential, logarithmic and simple combinations of some of these forms were investigated with respect to the data below the respective transition temperatures. Various functional forms for the heat capacity seem more or less successful over limited temperature ranges; however, no consistent patterns or trends emerged from these efforts. In the case of $Gd_2Fe_3Si_5$, described in Section III-B, there is a significant linear term in the heat capacity below the magnetic ordering temperature. This large linear contribution is evident over an extended temperature range (see Figure 13). A linear term in the heat capacity could be expected from 2-dimensional ferromagnetic spin waves (where the magnon dispersion relation is proportional to q^2) or from 1-dimensional antiferromagnetic spin waves (where the magnon dispersion relation is proportional to q). Since the magnetic structure of this compound is not known, one can only hypothesize about spin wave contributions to the heat capacity of $Gd_2Fe_3Si_5$.

V. CONCLUSIONS

The dependence of the antiferromagnetic ordering temperature on rare earth as depicted in Figure 20 agrees reasonably well with the ordering temperatures predicted by the de Gennes factor. This is especially true if only the lowest transition is considered for those materials in which more than one ordering temperature is observed. In ${\rm Tb}_{2}{\rm Fe}_{3}{\rm Si}_{5}^{55}$ and more recently $Er_2Fe_3Si_5$,⁶⁵ neutron diffraction experiments indicate the antiferromagnetic structure at the lowest temperatures is commensurate with the lattice while the magnetic structures at higher temperatures are incommensurate with the lattice. The critical behavior of the heat capacities of $Dy_2Fe_3Si_5$, $Ho_2Fe_3Si_5$ and $Er_2Fe_3Si_5$ as discussed in Section III and presented in Figures 22 and 23 further indicates the upper transition in compounds with multiple transitions is qualitatively different from the antiferromagnetic transition in those compounds with a single transition. Assuming the antiferromagnetic structure in each of the compounds with a single ordering temperature is also commensurate with the lattice, as seems likely, the ordering temperatures which should be compared to the de Gennes curve should be only the lowest ordering temperatures. In particular, there is no indication that dipole-dipole contributions play any significant role in determining the ordering temperatures as has been speculated.52

Figure 21 illustrates the large and systematic CEF effects in these compounds. In all cases except $Gd_2Fe_3Si_5$, a large fraction of the Hund's rules entropy is not recovered by 28 K. For example, only 40% of the Hund's rule entropy is recovered by 28 K in $Tb_2Fe_3Si_5$ and the fraction is

even smaller in the case of $Yb_2Fe_3Si_5$. In five of these compounds, the entropy at the highest antiferromagnetic ordering temperature is very nearly 0.5 R. This indicates that the ground state in these cases is a doublet. Thus, in each compound except $Gd_2Fe_3Si_5$, the ground state is split by the CEF to a doublet or in the case of $Tm_2Fe_3Si_5$ and $Yb_2Fe_3Si_5$ to two singlets within about 1 K. All other states lie at much higher temperatures. The doublet ground state occurs without regard to the number of electrons in the 4f-shell, in particular without regard to whether the number of electrons is even or odd.

The low symmetry of the rare earth site in this structure prohibits the development of a detailed energy level scheme based on the data available; however, some conclusions can be drawn about the nature of the ground state. As discussed in Section III-C, the ground state in these compounds is a doublet. Mössbauer data on $\text{Dy}_2\text{Fe}_3\text{Si}_5$ indicate a moment on Dy in this compound of 7.0 $\mu_{b},$ reduced from the Hund's rules values of 10.6 $\mu_{b}.$ This indicates that the ground state is not made up of pure $|+15/2\rangle$ and $|-15/2\rangle$ states but includes some admixture of lower J_z states. This makes the nearly de Gennes-like behavior of the ordering temperatures all the more puzzling since the effective angular momentum of the ground state doublet is expected to determine the ordering temperature and it is difficult to understand how, in general, any states other than the states of maximum J_{τ} $(|\pm 15/2\rangle$ in the case of $Dy_2Fe_3Si_5$) can produce an effective moment which varies in the same way as the Hund's rules moment. Thus, the de Gennes factor variation of the ordering temperatures is difficult to understand in view of the large CEF effects evident in these compounds.

Several distinctly different critical behaviors are observed in these compounds. Most striking is the set of transitions T_{M2} , T_{M3} and T_{M4} in $Er_2Fe_3Si_5$ indicated in Figure 17. The narrow width of these peaks and the sharpness of the high and low temperature sides of the feature as a whole indicate these are first order phase transitions. Recent neutron diffraction results indicate the feature at 2.34 K represents an incommensurate-commensurate magnetic transition.⁶⁵ The separate peaks in the heat capacity may represent ordering, as the temperature increases, to successively higher order commensurate phases until finally the incommensurate phase dominates.

The heat capacities of $Dy_2Fe_3Si_5$ and $Ho_2Fe_3Si_5$ are quite similar, even on close inspection. The apparent difference in the critical exponents above and below the ordering temperature is clearly demonstrated in Figures 22 and 23. Truly different critical exponents above and below the ordering temperature implies a discontinuity in the slope of the free energy and, therefore, a first order phase transition. An alternative possibility is that the apparent critical exponent of +1 above the ordering temperature only results from the smearing, possibly due to sample inhomogeneities, of a discontinuity in the specific heat as expected in mean field theories. In this case, the apparent critical exponent of +1 above the ordering temperature must be viewed as coincidental and not of any intrinsic importance. Either of these possibilities is unusual.

 $Sm_2Fe_3Si_5$, $Tm_2Fe_3Si_5$ and $Yb_2Fe_3Si_5$ exhibit what appear to be finite maxima in their heat capacities as compared to the singularities clearly

observed in the heat capacities of $Dy_2Fe_3Si_5$, $Ho_2Fe_3Si_5$ and $Er_2Fe_3Si_5$ and probably the singularities observed in $Gd_2Fe_3Si_5$ and $Tb_2Fe_3Si_5$. The heat capacities of $Tm_2Fe_3Si_5$ and $Yb_2Fe_3Si_5$ do not appear to diverge logarithmically as discussed in Sections III-G and III-H, respectively. $Sm_2Fe_3Si_5$ exhibits markedly rounded maxima in its heat capacity. Sample inhomogeneities may account for the finite maxima observed in the heat capacities of these compounds or the finite maxima may indicate mean field like behavior such as has been observed in $HoRh_4B_4$ and was suggested above for $Dy_2Fe_3Si_5$ and $Ho_2Fe_3Si_5$. $Yb_2Fe_3Si_5$ also exhibits anomalous curvature in its heat capacity above the magnetic ordering temperature. This may be attributed to an electronic Schottky-like anomaly arising from splitting of the ground state doublet in this compound.

Nuclear Schottky anomalies are observed in $Sm_2Fe_3Si_5$ and $Ho_2Fe_3Si_5$ which are larger and smaller, respectively, than expected from the observed anomalies in the respective rare-earth metals.⁶³ In the case of $Sm_2Fe_3Si_5$, the discrepancy is particularly large, indicating an effective magnetic field at the nucleus of 12 megagauss, as compared to an effective field of 3.3 megagauss observed in Sm metal. Such a large discrepancy in the observed effective magnetic field at the nucleus is difficult to understand even considering the large CEF effects evident in these materials. CEF effects are expected to have their major influence on the orbital angular momentum which is the principal source of the effective field at the nucleus in the rare earth elements. In the case of $Ho_2Fe_3Si_5$, CEF effects may well result in a reduced effective magnetic field at the nucleus as indicated by the reduced nuclear Schottky anomaly in this compound. No evidence can be found for superconductivity in the heat capacity of any of the antiferromagnetically ordered $\text{RE}_2\text{Fe}_3\text{Si}_5$ compounds. In particular, superconductivity in $\text{Tm}_2\text{Fe}_3\text{Si}_5$ as has been reported based on inductance and resistivity measurements³⁶ is not supported by the heat capacity results presented here. Based on previous heat capacity measurements in $\text{Lu}_2\text{Fe}_3\text{Si}_5$, $\text{Sc}_2\text{Fe}_3\text{Si}_5$ and $\text{Y}_2\text{Fe}_3\text{Si}_5$, the jump in the heat capacity at the reported superconducting transition of 1.7 K³⁶ for $\text{Tm}_2\text{Fe}_3\text{Si}_5$ is expected to be less than 3% of the observed total heat capacity of $\text{Tm}_2\text{Fe}_3\text{Si}_5$ at 1.7 K and may, therefore, be unobservable in these data. Therefore, while the heat capacity of $\text{Tm}_2\text{Fe}_3\text{Si}_5$ in no way indicates superconductivity, the possibility of superconductivity in $\text{Tm}_2\text{Fe}_3\text{Si}_5$ cannot be entirely ruled out.

VI. SUMMARY

The low temperature heat capacities of RE₂Fe₃Si₅ compounds reveal a number of important features of the magnetic order in these compounds. In agreement with previous work, 49-53 no evidence for a magnetic moment on the Fe is found. The systematics of the ordering temperatures as determined calorimetrically (Figure 20) indicate the principal mechanism by which the rare-earth atoms interact is the usual RKKY indirect exchange interaction. Several of these compounds exhibit multiple magnetic phase transitions, presumably due to anisotropy and/or next nearest neighbor interactions. The conduction electron-RE interaction strength is on the order of 0.03 eV which, while much smaller than typical interaction energies in the rare earth metals and binary intermetallic compounds, is larger than that observed in the ternary rhodium borides and the Chevrel-phase compounds which exhibit superconductivity in the presence of magnetic rare-earth atoms. No evidence for superconductivity can be found in the heat capacity of any of the $\text{RE}_2\text{Fe}_3\text{Si}_5$ compounds involving rare earth atoms with an incomplete 4f-shell. This is attributed to the strength of the magnetic interactions.

The anomalous critical behavior observed in these materials is quite unusual. A first order magnetic phase transition is indicated in $Er_2Fe_3Si_5$, and several other compounds exhibit critical behavior similar to that expected in mean field theory. A linear term in the heat capacity of $Gd_2Fe_3Si_5$ below the antiferromagnetic transition temperature suggests the possibility of an unusual spin way dispersion relation in this material.

GENERAL SUMMARY

These investigations have helped clarify many of the questions raised in the introduction while opening new areas for research. The heat capacity results on the superconducting compounds $Lu_2Fe_3Si_5$, $Sc_2Fe_3Si_5$ and $Y_2Fe_3Si_5$ suggest that not all of the conduction electrons participate in the superconductivity in these materials. The two-band model proposed is consistent with the large effects of alloying and pressure on the superconducting transition temperature as well as the heat capacity results reported here. A study of the heat capacity of a pseudo-ternary system such as $(Y_{1-x}Lu_x)_2$ Fe₃Si₅, in which T_c passes through a maximum and then drops to zero as x is increased from zero, 39 could further test the correctness of this model. Two major effects can be anticipated: 1) increased potential scattering from the disorder introduced on the rare-earth sublattice and 2) a movement of the Fermi-level due to the change in the lattice parameter on the introduction of a rare-earth of different atomic radii. The former effect is expected to introduce scattering between the hypothesized pockets of electrons. The fraction of electrons participating in the superconductivity can then be expected to increase, as the bands are no longer isolated, although since the "normal" band is expected to have a net repulsive electron-electron interaction, T_c will drop. The latter effect may either increase or decrease T_c, depending on whether the Fermi-level moves toward or away from a peak in the density of states of the "superconducting" band. It can be expected that the fraction of the electrons participating in the superconductivity will move with T_c , that is, increase when T_c increases

and decrease when T_c decreases, which can serve to differentiate this effect from the former effect.

The low temperature heat capacity measurements on the antiferromagnetic compounds $RE_{2}Fe_{3}Si_{5}$ (RE = Sm, Gd ~ Yb) reveal several features suggesting further studies. The various critical behaviors observed are quite unusual. Neutron scattering experiments and high resolution magnetization measurements on $Ho_2Fe_3Si_5$ and $Er_2Fe_3Si_5$ would be very useful in this respect. Questions such as the different critical exponents above and below the ordering temperature in Ho₂Fe₃Si₅ and the nature of the magnetic transitions T_{M2} , T_{M3} and T_{M4} (Figure 17) in $Er_2Fe_3Si_5$ are particularly interesting. Why do some of these materials exhibit multiple transitions while others do not? Are all of the magnetic transitions first order and if so, what is driving the transitions first order? Are the magnetic structures in $Sm_2Fe_3Si_5$, $Gd_2Fe_3Si_5$, $Dy_2Fe_3Si_5$, $Ho_2Fe_3Si_5$, $Tm_2Fe_3Si_5$ and Yb₂Fe₃Si₅ the same as either of the two known magnetic structures in this system, those of $\text{Tb}_2\text{Fe}_3\text{Si}_5$ and $\text{Er}_2\text{Fe}_3\text{Si}_5$? Recent Mössbauer measurements have allowed an estimate of the leading CEF terms and predicted ordering temperatures for the antiferromagnetic compounds in qualitative agreement with the observed trends in the ordering temperatures.⁶⁶

The report of superconductivity in $\text{Tm}_2\text{Fe}_3\text{Si}_5$ is not supported by the data presented here. As discussed previously, the heat capacity measurements cannot be considered conclusive in this respect, however, they do cast considerable doubt on the interpretation of the inductance and resistivity data previously reported.³⁶ An alternative possibility is that the presence of a small amount of a second phase in the sample of $\text{Tm}_2\text{Fe}_3\text{Si}_5$

previously reported is superconducting, and not the Tm₂Fe₃Si₅ phase itself. Attempts to isolate this second phase indicate this suggestion is correct although the data are not yet conclusive.

We believe this project demonstrates the potential of ternary compounds for yielding new and interesting low temperature states of matter. The systematic approach attempted here provides an opportunity for discerning trends which would not be possible if only a few of the ternary iron silicides had been studied. Only when a sufficient number of ternary systems have been thoroughly investigated can the systematics of the magnetic order and occurrence of superconductivity in ternary rare-earth compounds be considered well-understood.

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ACKNOWLEDGMENTS

It is difficult to give proper acknowledgments to all those people who have aided me since my arrival at Iowa State University. At this time, I would like to thank the entire Physics Department and Ames Laboratory faculty, staff, secretaries, technicians and fellow graduate students for all their efforts in my behalf. I thank Dr. Robert N. Shelton for giving me the time and space to make my own errors and for treating me as a fellow colleague. I would like to thank Herng-Er Horng, my classmate, for numerous useful discussions and help at important moments.

Without the constant presence and abilities of Peter Klavins, these projects would have taken considerably longer and perhaps not been quite so well done. I would like to thank Mike Sandholm, Dick Brown and Duke Sevde for lending their considerable experience and helping hands in the construction and maintenance of laboratory equipment. The aid of Marv Anderson and Dr. Clayton A. Swenson in calibrating required thermometers is greatly appreciated. The efficient and professional skills of Fran Laabs in providing microprobe results is greatly appreciated.

I would also like to acknowledge useful correspondence with Dr. Arnie Moodenbaugh and Dr. Hans Braun with regard to the $RE_2Fe_3Si_5$ -type compounds and Dr. Marco F. Pelizzone for performing the dc susceptibility measurements.

Finally and most importantly, I would like to thank my wife, Beth, for her tremendous patience and understanding and without whom none of this would mean so much.

APPENDIX: SOURCES AND PURITIES OF STARTING MATERIALS

Element	Source	Purity	
Si	Research Organic/Inorganic Chemical Corp.	9N lump	
Fe	Johnson Matthey Chemicals LTD	batch W.1471, 5N rod major impurities (weight): 	Pb 3 ppm Mg < 1 ppm Mn < 1 ppm Si < 1 ppm
		other impurities are all les	s than 1 ppm
Y	Ames Laboratory	batch 2276, ingot major impurities (atomic):	0 240 ppm Fe 46 ppm H 14 ppm C 11.5 ppm N 10.3 ppm C1 9 ppm W 7 ppm Cu 6.4 ppm Ce 4 ppm Gd 4 ppm
		other impurities are all les	s than 4 ppm
Sc	Ames Laboratory	batch 91278, ingot major impurities (atomic):	H 490 ppm 0 188 ppm W 84 ppm C 83 ppm Fe 53 ppm Lu 50 ppm F 28 ppm Ta 7.3 ppm N 6.4 ppm La 5 ppm Ce 4.2 ppm A1 3 ppm
		other impurities are all les	s than 3 ppm
Lu	Ames Laboratory	batch 51177, ingot major impurities (atomic):	0 33 ppm W 31 ppm Cu 20 ppm L 11 ppm Ni 10 ppm

Fe 6.1 ppm H 5 ppm other impurities are all less than 4 ppm batch 62973, ingot YЬ Ames Laboratory major impurities (atomic): 0 38 ppm Fe 30 ppm Ca <10 ppm C 10 ppm H 8 ppm Lu 7 ppm La 6 ppm Gd 6 ppm other impurities are all less than 3 ppm batch 32878, ingot Ames Laboratory Tm major impurities (atomic): Fe 25 ppm C 24 ppm F 14 ppm Cu 11 ppm C1 10 ppm Ce 8 ppm Fe 6.2 ppm Si 3 ppm other impurities are all less than 3 ppm batch 71177, ingot Er Ames Laboratory major impurities (atomic): Ta 42 ppm 0 35 ppm C 10 ppm Fe 6.6 ppm H 6 ppm Fe 6 ppm Cu 3.6 ppm other impurities are all less than 4 ppm batch 9977, ingot Но Ames Laboratory major impurities (atomic): F 75 ppm Fe 45 ppm 0 30 ppm Ta 30 ppm C 22 ppm Hf 6 ppm Cr 5 ppm Cu 3.4 ppm other impurities are all less than 4 ppm

batch 1578, ingot Dy Ames Laboratory major impurities (atomic): F 74 ppm 0 36 ppm Ta 30 ppm Fe 10 ppm C 8 ppm C1 5 ppm Mn 4 ppm other impurities are all less than 4 ppm batch 42178, ingot Tb Ames Laboratory major impurities (atomic): 0 66 ppm C 42 ppm Fe 42 ppm Cu 19 ppm Gd 11 ppm F 8 ppm N 8 ppm Ce 7 ppm H 5 ppm C1 4 ppm other impurities are all less than 4 ppm batch 3579, ingot Gd Ames Laboratory major impurities (atomic): 0 38 ppm Fe 25 ppm Zr 9 ppm C 8 ppm W 5 ppm H 4 ppm Al 4 ppm K 4 ppm other impurities are all less than 3 ppm batch 32379, ingot
major impurities (atomic): Ames Laboratory Sm 0 37 ppm As 80 ppm Ta 80 ppm H 17 ppm Nd 67 ppm Ca 30 ppm C 9 ppm Ce 14 ppm La 8.4 ppm Pr 6 ppm other impuruties are all less than 4 ppm