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Investigation of non-magnetic iron in Lu$_2$Fe$_3$Si$_5$-type superconductors

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Iowa State University, 1987
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Investigation of non-magnetic iron in
Lu$_2$Fe$_3$Si$_5$-type superconductors

by

Youwen Xu

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

Department: Physics
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In Charge of Major Work

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1987
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I. INTRODUCTION

A. General Background on Superconductivity

The phenomenon of superconductivity has been studied for over 70 years since its first discovery by Kamerlingh Onnes\(^1-4\), in Leiden in 1911. The most striking features of a superconductor are:

1) The absence of any measurable dc electrical resistivity. When the temperature of a superconductor is lowered below a certain value, it loses all its electrical resistivity. This characteristic temperature is called the superconducting transition temperature \(T_c\). An experiment was done by S. C. Collins\(^5\) in which a superconducting ring carrying an induced current was kept below \(T_c\) for two and a half years. No decay of current was detected during this period. The upper limit of resistivity of the superconductor is lower than \(10^{-23} \text{ ohm-cm}\) (Ref. 6).

2) A superconductor can be a perfect diamagnet provided that the magnetic field is not too strong. A surface electric current, induced by the applied magnetic field, can produce a magnetic field exactly cancelling the applied field in the interior of the superconductor. Inside the superconductor, \(B=0\). It behaves like the magnetic field is pushed out. This is called the Meissner effect. The magnetic field which can destroy the superconductivity is called the critical magnetic field \(H_c\).

3) There is usually an energy gap of width \(2\Delta\) centered at the Fermi level. An electron can be extracted from a superconductor only if its
energy $\epsilon-\epsilon_F$ exceeds $\Delta$. The energy gap varies with temperature. $\Delta$ has its maximum value at $T=0$ and vanishes at $T=T_C$. In specific heat measurements, the heat capacity, $C$, jumps to a higher value at $T=T_C$ and decreases exponentially to the value well below what one would expect for the normal, non-superconducting state.

There have been numerous theoretical efforts aimed at the explanation of superconductivity. In 1935, the brothers London proposed two equations which describe the perfect conductivity and the Meissner effect. Their model is based on a point by point relation between the current density and vector potential associated with a magnetic field. The Londons' theory provided useful tools in the semi-quantitative analysis of many superconducting problems and predicted that the current and the magnetic field can exist in a superconductor only within a thin layer of thickness $\lambda_L$. The two equations proposed by the Londons are known as the London equation; and $\lambda_L$ is known as the London penetration depth.

In 1950, Ginzburg and Landau developed a method of treating superconductivity as a macroscopic quantum state described by a complex order function $\psi$. This function is a kind of "effective" wave function of the superconducting electrons. $|\psi|^2$ equals the density of the superconducting electrons. $\psi$ thus vanishes above $T_C$. Ginzburg's and Landau's theory has been applied successfully to explain many experimental results.

In 1953, A. B. Pippard modified the London equations by taking into account the finite coherence of the superconducting wave functions. A new quantity, the coherence length $\xi$, was introduced which is a
measure of the non-locality of the superconducting electrons. By this generalization, the simple London equations can be used with this modification in many instances.

In 1957, beginning with the Ginzburg-Landau theory, A. A. Abrikosov\textsuperscript{13} classified superconductors into type I and type II. Those superconductors with $K = \sqrt{\xi} \ll 1$ are called type I superconductors, while those with $K \gg 1$ are called type II superconductors. The major difference between these two types of superconductors is that there exists a mixed state in a type II superconductor when the applied magnetic field is between two certain values, namely the upper and lower critical field. Today most of the superconducting elements are known to be type I, while superconducting compounds are known to be type II.

It was found in 1950\textsuperscript{14,15} that for many superconducting elements the critical temperature $T_C$ depends on the isotopic mass. This isotopic effect suggested the importance of phonon participation in the phenomenon of superconductivity.

In light of these experimental and theoretical advances, in 1957, Bardeen, Cooper and Schrieffer\textsuperscript{16} established the most important and successful theory of superconductivity. This theory showed that through the interaction with phonons, in the neighborhood of the Fermi surface, each electron is paired with one of opposite spin and momentum to condense into a bound state of lower energy. This kind of electron pair is called a Cooper pair. An energy gap exists to separate the state with the largest number of Cooper pairs from the state with one pair less. The major quantitative prediction of the BCS theory are:

1) The transition temperature of superconductivity $T_C$ is related to the density of states of the electrons at the Fermi level $N(E_F)$ as:
\[ T_c = 1.13 \Theta_D e^{-\frac{1}{N(E_F)V}} \] (1)

where \( \Theta_D \) is the Debye temperature and \( V \) is the electron-phonon coupling constant which measures the strength of the electron-phonon interaction giving rise to superconductivity.

2) The zero field energy gap \( \Delta(T) \) vanishes at \( T_c \) according to:

\[ \frac{\Delta(T)}{\Delta(0)} = 1.74 \left( 1 - \frac{T}{T_c} \right)^2 \] (2)

for temperatures close to \( T_c \). \( \Delta(0) \) is the energy gap at \( T=0 \).

3) The thermodynamic critical field \( H_c(T) \) is expressed in a form:

\[ \frac{H_c(T)}{H_c(0)} = 1 - \left( \frac{T}{T_c} \right)^2 \] (3)

where \( H_c(0) \) is the thermodynamic critical field at \( T=0 \).

4) The specific heat jump at the transition temperature \( T_c \) follows:

\[ \frac{C_s - C_n}{\gamma_n \frac{T_c}{T}} = 1.43 \] (4)

where \( \gamma_n \) is the coefficient of the electronic contribution term in the normal state heat capacity.

These BCS predictions have been shown to be in good agreement with many experimental results except for the "strong coupling" superconductors. The BCS theory successfully explained the major electromagnetic and thermal properties of superconductors, and it is universally accepted as the fundamental microscopic theory of superconductivity.
Since in the BCS theory, the interaction between the electrons and phonons is assumed to be weak, and the interactions between the quasiparticles are neglected, the BCS theory is also called the "weak coupling" theory of superconductivity.

In order to understand the behavior of the "strong coupling" superconductors, G. M. Eliashberg\(^{17,18}\) in 1960 proposed a theory in which \( T_c \) is related to the quantities \( \lambda, \mu^\ast, \) and \( \Theta_D. \) \( \lambda \) is the electron-phonon coupling constant and \( \mu^\ast \) is the Coulomb repulsion term. For strong coupled superconductors \( \lambda=1 \) while for weak coupled superconductors \( \lambda<<1. \)

In 1968, McMillan\(^{19}\) numerically solved Eliashberg's equation and obtained an analytic function which can be used to calculate the superconducting transition temperature \( T_c \) of a metal according to given properties of the normal state. In McMillan's formulation, \( T_c \) is related to the electron-phonon coupling constant \( \lambda \) and a Coulomb coupling (electron-electron coupling) constant \( \mu^\ast \) in a form:

\[
T_c = \frac{\Theta_D}{1.45} \exp \left[ - \frac{1.04(1+\lambda)}{\lambda - \mu^\ast(1+0.62\lambda)} \right]
\]  

(5)

In relation to the BCS expression \( N(E_F)V \), the net attractive interaction for superconductivity becomes \( \lambda-\mu^\ast \), instead of \( N(E_F)V \). Thus Equation(5) reduces roughly to Equation (1) in the limit \( \lambda<<1. \) McMillan's formula has been applied extensively to the analysis of strong and intermediate coupled superconducting systems and yielded results in remarkably good agreement with experimental data.

All of the theoretical and experimental results mentioned above contributed greatly to our current understanding of superconductivity.
However, the recent discovery of very high $T_c$ superconducting oxides has raised new questions about this topic and challenged scientists to develop a more advanced theory to explain this fascinating phenomenon.

B. Ternary Superconductors

Realizing the important implications of superconductivity for electrical technology, scientists put a great deal of effort into searching for new superconducting materials with higher transition temperatures. After numerous experimental work, all the elements have been studied. A list of the superconducting elements in a form of periodic table can be found in review papers and basic solid state text books. Binary alloys were also studied. The cubic NaCl type (B1) structure, the MgCu$_2$ type (C15 or Laves phase) structure, and the $\beta$-W type (A15) structure are important classes of superconductors. Among them, A15 compounds attracted most of the attention in the past 20 years because up to 1986, the highest transition temperature was found in A15 compounds: V$_3$Si ($T_c=17K$), Nb$_3$Sn ($T_c=18K$), Nb$_3$Ge-Nb$_3$Al ($T_c=20K$), Nb$_3$Ga ($T_c=20.3K$) and Nb$_3$Ge film ($T_c=23K$). From the discovery of Nb$_3$Ge with $T_c=23K$ in 1973 to 1986, the superconducting transition temperature was not raised any higher. During this period, scientists turned their attention to the ternary compounds. The motivation is that in ternary compounds, there are distinct crystallographic sites for each of the three elements. Thus scientists would have increased freedom to substitute for the third atom. The intense study of ternary superconductors started when
Matthias and coworkers discovered two important classes of ternary superconductors, namely, the triclinic chevrel phases $\text{M}_x\text{Mo}_6\text{X}_8$ (Ref. 36) and the tetragonal borides $\text{MRh}_4\text{B}_4$ (Ref. 37,38). In the former class, $\text{M}$ can be any of a large number of metal atoms including rare earths (RE)$_3^{38,39}$, and $\text{X}$ is a chalcogen. In the latter class, $\text{M}$ can be thorium, or one of ten rare earth atoms$^{40,41}$. It was found that the chevrel phase compound $\text{PbMo}_6\text{S}_8$ exhibited the highest upper critical magnetic field $^{42-44} (H_{c2}(0)=60$ tesla) known at that time. Another two compounds $\text{ErRh}_4\text{B}_4$ (Ref. 45) and $\text{HoMo}_6\text{S}_8$ (Ref. 46) show re-entrant superconductivity, that is, they become superconducting when cooling to $T_{c1}$ and at a lower temperature $T_{c2}$, reenter a normal state with the onset of ferromagnetic ordering. Most surprisingly, in both chevrel phase and tetragonal borides compounds, when $\text{M}$ is a magnetic rare earth, superconductivity still occurs even when the rare earth concentration is as high as 7 at.% in the former class and 11 at.% in the latter class$^{38-40}$. The rare earth atoms form a spatially ordered array in these two structures. Thus superconductivity and long range magnetic ordering exist at the same time. This was never observed in any superconducting elements or binary alloys. The coexistence of superconductivity and long range magnetic ordering in the ternary superconductors provided scientists an opportunity to study the relation between the two.

C. Ternary Compounds RE$_2$Fe$_3$Si$_5$

Because of the unique properties that ternary superconducting compounds exhibit, scientists continued to search for new
superconducting materials with similar properties. Up to 30 different structures of ternary compounds have been found to contain superconductors\textsuperscript{47}. Among them, the RE\textsubscript{2}Fe\textsubscript{3}Si\textsubscript{5} and Sc\textsubscript{5}Co\textsubscript{4}Si\textsubscript{10} showed unusual behavior in that, in spite of the presence of a large percentage of Fe and Co, Sc\textsubscript{5}Co\textsubscript{4}Si\textsubscript{10} becomes superconducting at 5 K\textsuperscript{48,49} while four RE\textsubscript{2}Fe\textsubscript{3}Si\textsubscript{5} compounds (RE=Sc, Y, Tm, Lu) were reported superconducting above 1 K\textsuperscript{50-53}. Fe and Co are usually considered as ferromagnetic elements which do not favor superconductivity. For example, dissolved iron in chevrel phases or A15 phases depresses rapidly the superconducting transition temperature\textsuperscript{54,55}. In addition, in RE\textsubscript{2}Fe\textsubscript{3}Si\textsubscript{5} compounds, Fe appears to be crucial for the superconductivity because when Fe is replaced by the isoelectronic metals Ru and Os, the isostructural compounds Lu\textsubscript{2}Ru\textsubscript{3}Si\textsubscript{5} and Y\textsubscript{2}Os\textsubscript{3}Si\textsubscript{5} show no superconducting transition above 1 K (Ref. 56). Other interesting properties RE\textsubscript{2}Fe\textsubscript{3}Si\textsubscript{5} compounds possess are:

1) When rare earth elements with an unfilled 4f-shell are in the RE site, the compound RE\textsubscript{2}Fe\textsubscript{3}Si\textsubscript{5} orders magnetically at temperatures below 11 K\textsuperscript{57-59}.

2) In superconducting compounds Sc\textsubscript{2}Fe\textsubscript{3}Si\textsubscript{5} and Lu\textsubscript{2}Fe\textsubscript{3}Si\textsubscript{5}, when a small amount of Sc and Lu is replaced by the non-magnetic element yttrium, or when a small amount of Lu is replaced by Sc, T\textsubscript{c} is depressed as rapidly as for magnetic rare earth substitution\textsuperscript{60}.

3) Tm\textsubscript{2}Fe\textsubscript{3}Si\textsubscript{5} shows re-entrant superconductivity. This compound becomes superconducting at T\textsubscript{c1}=1.7 K and then re-enters the normal state with antiferromagnetic ordering at a lower temperature (T\textsubscript{c2}=1.1 K)\textsuperscript{52} showing the competition between superconductivity and magnetic ordering.
4) The superconducting transition temperature $T_c$ of compounds $\text{RE}_2\text{Fe}_3\text{Si}_5$ ($\text{RE} = \text{Sc}, \text{Y}, \text{Lu}, \text{Tm}$) shows a marked non-linear pressure dependence. For $\text{Lu}_2\text{Fe}_3\text{Si}_5$ and $\text{Sc}_2\text{Fe}_3\text{Si}_5$, $T_c$ decreases non-linearly; while for $\text{Y}_2\text{Fe}_3\text{Si}_5$, $T_c$ increases with pressure from 2.3 K to almost 5 K at $P = 15$ kbar and decreases slowly as pressure continues to increase. The superconducting transition temperature, $T_{c1}$, of $\text{Tm}_2\text{Fe}_3\text{Si}_5$ has an unusually strong pressure dependence with $dT_{c1}/dP = 0.47$K/kbar at low pressure. This was the largest known derivative at the time. The pressure dependence of $T_{c1}$ is non-linear, $T_{c1}$ is first raised to 3K at $P = 9$ kbar and then decreased as pressure increases.

5) The heat capacity of the superconducting compounds $\text{Sc}_2\text{Fe}_3\text{Si}_5$, $\text{Y}_2\text{Fe}_3\text{Si}_5$ and $\text{Lu}_2\text{Fe}_3\text{Si}_5$ has an anomalously large $T^5$ dependence in the normal state. In the superconducting state, the heat capacity has a non-zero, large linear term indicating a fraction of the energy band remains normal below $T_c$.

6) Mössbauer studies on $\text{RE}_2\text{Fe}_3\text{Si}_5$ showed that the magnetic moment of the iron atoms in these compounds is less than 0.03$\mu_B$. When the RE atom orders magnetically, the Fe atoms remain non-magnetic in zero applied field. When the applied magnetic field is not zero, a small moment is observed at the Fe site which opposes the field.

The above mentioned special properties of $\text{RE}_2\text{Fe}_3\text{Si}_5$ pose interesting questions about the origin of the superconducting electrons, and the formation of magnetic moments of 3d-transition metals in the superconducting hosts.
The motivation of this work is to investigate the non-magnetic behavior of the iron atoms in Lu$_2$Fe$_3$Si$_5$-type compounds. Crystallographic analysis shows that the structure of these compounds is primitive tetragonal-type$^{50,56}$. Fe atoms in this structure form two types of "clusters" (see III.A). The Fe-Fe intracluster distances are 2.64Å and 2.67Å, larger than the interatomic distance 2.48Å in iron metal, while the intercluster Fe-Fe distances are quite large, 4.10Å. The coordination numbers of the two iron sites are 13 and 12. The interatomic distances between Fe and its nearest neighbor Si atoms are much smaller than the sum of their metallic radii. It was suggested that the quenching of the magnetic moment of iron in RE$_2$Fe$_3$Si$_5$ occurs because of 1) the lack of symmetry of the nearest neighbor configuration$^{65}$, 2) the relatively large Fe-Fe interatomic distances$^{50}$, 3) the strong covalent bonding between the Fe and Si atoms$^{63}$.

In order to clarify the origin of the non-magnetic behavior of iron atoms in the compounds RE$_2$Fe$_3$Si$_5$, we chose Lu$_2$Fe$_3$Si$_5$ as our "pure" sample, and replaced Fe atoms by other transition metals: Cr, Mn, Co, Ni, Cu, and Ru. Among these transition metals, Cr, Mn, Co and Ni all have an unfilled 3d-shell, while Cu has a filled 3d-shell. Ru, a 4d-transition metal, has the same electronic structure as Fe, i.e., the number of electrons outside the filled inert-gas core is the same. We made samples with 1.0 and 2.0 at.% Fe replaced by each of the above mentioned transition metals, and with 4, 6, 8, 10, 20, 25, 35 at.% Ru and Co substitutions, and finally replaced Fe completely by Co and Ru.
The physical properties we measured were: 1) lattice parameters, 2) superconducting transition temperature, 3) electrical resistivity, 4) magnetic susceptibility, 5) low temperature heat capacity. The experimental details are given in Chapter II, the results and discussions are in Chapter III. Finally, in Chapter IV, we give the concluding remarks of this investigation.
II. EXPERIMENTAL DETAILS

A. Sample Preparation

All samples were prepared from high purity elements by arc-melting in a Zr gettered argon atmosphere. The purity of each element used is listed in the Appendix. Each sample weighed about 1 gram, while those samples made for heat capacity measurement were approximately 3 grams. Lu, Fe and the transition-metal additions were melted together, turned over remelted, then Si was melted into this mixture. Since small segments often were ejected from the sample during the cooling off, the arc flame was held on the sample for longer than one minute when Si was melted into the metal alloy in order to promote the best homogeneity. By this prolonged melting, the sample achieved stoichiometric composition after the initial introduction of Si. The sample was then turned over and remelted 3 or 4 times. The mass loss was usually greater than 5% after melting as a result of cracking and lost pieces. The as-cast ingots were shiny, beautifully faceted and very brittle. There were usually some cracks on the surface of the sample.

The sample was sealed in a quartz tube in an argon atmosphere of 230 Torr and heat treated at 1250°C for 4 days followed by annealing at 800°C for 7 days. The sample was water quenched to room temperature after the annealing. A very thin oxide layer on the surface of the sample was removed by polishing with sandpaper.
B. Crystallographic Analysis

To confirm that the samples belong to the Sc$_2$Fe$_3$Si$_5$-type phase and to calculate the lattice parameters of the crystal, a small part of each sample was ground into powder and characterized by taking powder X-ray diffraction measurements on a RIGAKU diffractometer with a copper target and a graphite monochromator. The diffractometer was controlled by a microcomputer. Step-scan with a rate of 0.01°/sec was used. A 16 point smoothing function was applied to the raw data. The angular position of the diffraction peaks was defined as the mid-point of the peak width. A program named FINAX was used to generate the theoretical powder diffraction pattern of a structure according to the given atomic positions, space group and estimated lattice parameters. This same program was used to least square fit the measured diffraction patterns to the theoretical one and calculate the lattice parameters of the measured crystal. The diffraction patterns of each sample with an internal silicon standard mixed in were compared with the FINAX output for the stoichiometric Lu$_2$Fe$_3$Si$_5$ and indexed. The lattice parameters of each sample were then calculated accordingly.

C. Magnetic Property Measurements

Static magnetic susceptibility measurements were performed on a susceptometer called Model MPMS from Quantum Design Inc. It is a sophisticated analytical instrument designed especially for the study of
the magnetic properties of small experimental samples. This system is fully automated with computer control of the following components: 1) superconducting magnet system which provides a constant magnetic field to a maximum value of ± 5.5 tesla, 2) a temperature control system which enables the user to measure in a temperature range from 2.0K to 400K with an accuracy of 0.1%, 3) an automatic sample transport system to move the sample in the magnetic field, 4) a SQUID detector system to detect the flux change in the detector coil caused by the moving sample. All controls and user interface are through a HP-150II touch screen computer which also provides some analysis of the data. Repeat measuring on the same sample showed the reproducibility was better than 5%. A cross section of the sample measuring region is shown in Figure 1.

D. Superconducting Transition Temperature Measurements

Superconducting transition temperatures were measured by monitoring the low frequency ac susceptibility of the samples. The measuring temperature ranges from 1.2K to 30K and was monitored by means of a calibrated Ge resistance thermometer with an accuracy of 0.1%. The measuring frequency was 25 Hz and the peak measuring field was about 6 Oe. For samples with a transition temperature $T_c$ lower than 1.2K, the $T_c$'s were measured on a commercial He³-He⁴ dilution refrigerator from Biomedical Technologies Inc. The $T_c$ was defined as the midpoint of the transition, and the transition width was defined as the temperatures when the inductive signal achieved 10% and 90% of the full transition value.
Figure 1. The cross section of sample measuring system of the susceptometer
E. Electrical Resistivity Measurements

The dc electrical resistivity of the samples were measured in a Model MPMS dewar which has a temperature control system similar to the one described previously. A Keithley model 228 current source was used to provide a constant current for the measurement and a Keithley model 181 nanovoltmeter was used to measure the output voltage.

A large portion of the ingot sample to be measured was polished into a small parallelepiped with a cross section approximately $1 \times 1\text{mm}^2$ and a length 1.3 to 3.4mm depending on the size and the quality of the original ingot. To avoid having cracks inside the sample ingot to be measured, one needed to frequently examine the polished surface under an optical microscope when polishing. Four platinum wires ($d=0.05\text{mm}$) were spot-welded onto the sample, two on the ends as the current leads and two on the sides as the voltage leads (see Figure 2). A small direct current of 10mA was applied during the measurement to minimize the electrical heating. The current was applied in both directions for each measurement, and the voltage $(V_+ - V_-)/2$ was used to calculate the resistance. Since the current source, the nanovoltmeter, and the temperature control system all have standard IEEE interfaces, the dc electrical resistivity measurement was fully automated. A HP-85 computer was equipped to control the whole system and perform data acquisition and analysis.
Figure 2. Electrical resistivity measurement

current source

nanovoltmeter
F. Specific Heat Measurements

The low temperature specific heat of the samples was measured at temperatures ranging from 0.6°K to 30°K by means of a heat-pulse type semi-adiabatic calorimeter. The details of the design and the measurement procedure are given in ref. 67 and 68. The major features of the system are: 1) continuously operating He\(^4\) pot and He\(^3\) pot which can maintain the system at a temperature below 1.2K for at least 4-5 hours or above 1.2K for days, 2) a mechanical heat switch between the He\(^3\) pot and the sample holder serves to cool the sample down without exchange gas, 3) a thin-walled, rigid, low-thermal-conductivity nylon support provides a good mechanical stability and a thermal shield with a heater provide the temperature control.

A 1kΩ Pt-W heater wound on the sample holder gave the sample a heat pulse of approximately duration 9 seconds for each measurement. The temperature change of the sample during each pulse was determined by monitoring the conductance of the sample’s Ge resistance thermometer on a strip chart recorder. The error in the sample’s heat capacity was believed to arise mainly from this graphic procedure. A programmable HP-97 calculator calculated the total heat capacity of the sample and its holder utilizing the parameters obtained for each data point. From the total heat capacity, the specific heat of the sample was calculated and analyzed later by a general heat capacity program.
III. RESULTS AND DISCUSSIONS

A. Lattice Parameters

In 1977, O. I. Bodak et al.\textsuperscript{69} first analyzed the crystal structure of Sc$_2$Fe$_3$Si$_5$. Their analysis showed that Sc$_2$Fe$_3$Si$_5$ has a tetragonal structure with space group P4/mnc. Later, in 1979, H. F. Braun\textsuperscript{50} replaced Sc by the lanthanide series rare earth elements, samarium through lutetium, and he found that all RE$_2$Fe$_3$Si$_5$ (RE=rare earth) have the same tetragonal-type structure except europium. The structure of Lu$_2$Fe$_3$Si$_5$ was refined by B. Chabot\textsuperscript{70} in 1984 using single crystal data. His result for the lattice parameters and the atomic positions (Table 1) were used in this investigation to calculate the theoretical x-ray powder diffraction patterns for the stoichiometric Lu$_2$Fe$_3$Si$_5$.

The lattice parameters of all the samples in this investigation were refined according to their x-ray powder diffraction patterns. The x-ray diffraction showed that there was a small amount of Lu$_2$O$_3$ in a few samples. Most of the samples did not have more than 2\% impurities, the lower limit of detectibility of our system. As more transition metals were substituted for Fe, the reflection lines shifted in position but no second phase appeared up to 10 at.\% substitution. The micrographs taken under an optical microscope at a magnification 250x revealed that the sample was single phased until 12 at.\% Co was reached (see Figure 3).
Table 1. Crystallographic data for Lu$_2$Fe$_3$Si$_5$ (Ref. 70)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>symmetry</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(1)</td>
<td>8h</td>
<td>m</td>
<td>0.0231(7)$^a$</td>
<td>0.3188(8)</td>
<td>0</td>
</tr>
<tr>
<td>Fe(1)</td>
<td>8h</td>
<td>m</td>
<td>0.1428(4)</td>
<td>0.1228(4)</td>
<td>0</td>
</tr>
<tr>
<td>Lu</td>
<td>8h</td>
<td>m</td>
<td>0.2625(1)</td>
<td>0.4306(1)</td>
<td>0</td>
</tr>
<tr>
<td>Si(2)</td>
<td>8g</td>
<td>2</td>
<td>0.1786(5)</td>
<td>0.6786(6)</td>
<td>1/4</td>
</tr>
<tr>
<td>Si(3)</td>
<td>4e</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0.249(2)</td>
</tr>
<tr>
<td>Fe(2)</td>
<td>4d</td>
<td>222</td>
<td>0</td>
<td>1/2</td>
<td>1/4</td>
</tr>
</tbody>
</table>

$^a$The estimated standard deviations are given in the parentheses.
Figure 3. Micrographs of the Lu₃(Fe₁₋ₓCoₓ)Si₅ (Magnification 250)
upper: x=0.10; lower: x=0.12
For this sample, the second phase was Lu₂Co₃Si₅ which has a monoclinic structure. The Lu₂Ru₃Si₅ crystallizes in the tetragonal Sc₂Fe₃Si₅-type structure as well, therefore, the sample remained in single phase across the entire series Lu₂(Fe₁₋ₓRuₓ)₃Si₅.

Table 2 lists the measured lattice parameters for each sample. From the table one can see that the changes in lattice constants were small. After 10 at.% Fe was replaced by Co, the lattice constant a decreased 0.15% while c increased 0.09% resulting in a unit cell volume decrease of 0.17%. For 10 at.% Ru replacement, a increased 0.29% and c increased 0.2%; thus, the unit cell volume increased 0.77%. These changes in the lattice parameters were basically the same in magnitude as the changes in atomic radii for each element (Table 3). For Cr, Mn, and Ru with atomic radius greater than that of Fe, the lattice parameters increased; while for Co and Ni with smaller atomic radii, the lattice parameters decreased. Table 4 lists the interatomic distances of the Lu₂Fe₃Si₅ compound. One ought to notice that the distances between the iron atoms and their nearest neighbors were considerably shorter than the sum of their atomic radii. This indicates the presence of strong covalent bonding between the atoms. Such kind of a covalent bonding plays an important role in the non-magnetic properties of the 3-d transition-metals in this compound. This will be discussed later.

Figure 4 is a projection along the c-axis of the unit cell of the Lu₂Fe₃Si₅ compound. The iron atoms occupy two distinct crystallographic sites in this structure. Two thirds of them form squares in a plane perpendicular to the c-axis and centered at the (0,0) and (1/2,1/2)
Table 2. Lattice Parameters for Lu$_2$(Fe$_{1-x}$T$_x$)$_3$Si$_5$

(T=Cr, Mn, Co, Ni, Cu, Ru)

<table>
<thead>
<tr>
<th>at.%</th>
<th>a(Å)</th>
<th>c(Å)</th>
<th>c/a</th>
<th>V(Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>10.344(1)$^a$</td>
<td>5.386(1)</td>
<td>0.5207</td>
<td>576.3(1)</td>
</tr>
<tr>
<td>0.5 Cr</td>
<td>10.343(1)</td>
<td>5.385(1)</td>
<td>0.5206</td>
<td>576.0(1)</td>
</tr>
<tr>
<td>1.0 Cr</td>
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<td>5.384(1)</td>
<td>0.5203</td>
<td>576.4(2)</td>
</tr>
<tr>
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<td>10.346(1)</td>
<td>5.386(1)</td>
<td>0.5206</td>
<td>576.2(1)</td>
</tr>
<tr>
<td>1.5 Mn</td>
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<td>5.386(2)</td>
<td>0.5206</td>
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<tr>
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$^a$The numbers in the parentheses are the estimated standard deviations in units of the least significant digit.
Table 2 (continued)

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<th>Vol. (Å³)</th>
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Table 3. Metallic radii of elements Cr, Mn, Fe, Co, Ni, Cu, and Ru (Ref. 73)

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<td>Fe</td>
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Table 4. Interatomic Distances \( d \leq 3.12 \text{ Å} \) and rounded values \( \delta = 100(d - Er)/Er \) for Lu\(_2\)Fe\(_3\)Si\(_5\) (The atomic radii used: \( r_{Lu} = 1.734 \text{ Å}, \)
\( r_{Fe} = 1.274 \text{ Å}, r_{Si} = 1.319 \text{ Å} \) (Ref. 70)

<table>
<thead>
<tr>
<th></th>
<th>( d(\text{Å}) )</th>
<th>( \delta(%) )</th>
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<tr>
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<td>-2Si(1)</td>
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\(^a\)The standard deviations are given in the parentheses.
Figure 4. Atomic structure of compound Lu$_2$Fe$_3$Si$_5$. Projection on the xy plane.
Figure 5. Lattice parameters of the Lu$_2$(Fe$_{1-x}$Co$_x$)Si$_5$ compounds
Figure 6. Lattice parameters of the Lu$_2$(Fe$_{1-x}$Ru$_x$)Si$_5$ compounds I
Figure 7. Lattice parameters of the Lu$_2$(Fe$_{1-x}$Ru$_x$)Si$_5$ compounds II
position. One third form Fe chains parallel to the c-axis. The
distances between the Fe atoms in the squares and the chains are 2.64Å
and 2.67Å respectively. The greatest reticular density is along the
[110] direction. This correlates with the change in lattice constant a
being greater than the change in c when Fe is replaced by other metals.

Figures 5 and 6 present the linear relationship between the lattice
parameters and the corresponding Co and Ru concentration up to 10 at.%. The error bars represent the estimated standard deviation. Figure 7
shows the increase of lattice parameters across the entire series
\( \text{Lu}_2(\text{Fe}_{1-x}\text{Ru}_x)\text{Si}_5 \). The measured lattice parameters of the \( \text{Lu}_2\text{Ru}_3\text{Si}_5 \) compound are in excellent agreement with those given in ref. 56.

B. The Superconducting Transition Temperature

It is known that the superconducting transition temperature of a
material will be changed when impurities are added because of the
interaction between the conduction electrons and the impurity atoms. There are two basic kinds of impurities; one is a magnetic impurity
which has a localized magnetic moment, the other is a non-magnetic
impurity in which the localized magnetic moment is not present. If the
impurity has a localized magnetic moment, the exchange interaction
between the conduction electrons and the spin of impurity atoms affects
the conservation of the electron spin, breaks the Cooper pairs, and
lowers the transition temperature. If the impurity does not have a
localized magnetic moment, there are two factors which may affect the
transition temperature. One of them is the scattering of electrons from
a broad non-magnetic impurity state. The other is the Coulomb repulsion two members of the Cooper pair suffer when they are scattered into an impurity state where localized spin fluctuation are present. Both weaken the formation of Cooper pairs due to the electron-phonon interaction, and result in the decrease of the transition temperature.

The effects of magnetic impurities and non-magnetic impurities are very different in terms of the detailed behavior of $T_c$ versus impurity concentration $x$.

Abrikosov and Gor'kov in 1960 established a theory which explained the effect of paramagnetic impurities on superconductors. Their calculation showed that the dependence of the transition temperature on the impurity concentration is the derivative of the logarithm of a $T$-function. When the impurity concentration is very low ($x < 1 \text{ at.\%}$), $T_c$ decreases proportional to $x$. The overall curve of $T_c$ versus $x$ has a negative curvature. The rapid decrease of $T_c$ with $x$ leads to a low critical concentration at which the superconductivity does not occur at any temperature. This theory has been verified by a number of experiments.

When transition metals are added into a superconducting compound as impurities, the d-electrons can hybridize with the conduction electron state of the matrix to form a localized magnetic resonance state. When the resonance is narrow ($\Delta < k_B T_{co}$), localized magnetic moments will be formed at the impurity sites. In this instance, the effect of transition metal impurities on $T_c$ follows the Abrikosov-Gor'kov theory. If the d-resonance is broad, there will be no localized magnetic moment formed at the impurity site, and the transition metal behaves like a
Kaiser made a detailed self-consistent calculation for the effect of non-magnetic localized states in superconducting alloys. Kaiser assumed that the host matrix is a BCS superconductor with the superconducting transition temperature:

$$T_c = 1.13 \frac{1}{\Theta_D} \left( e^{\frac{1}{\Theta_D}} - e^{\frac{1}{N(E_F)V}} \right)$$

Where \( \Theta_D \) is the Debye temperature, \( N(E_F) \) is the density of states of the conduction electrons at the Fermi level, and \( V \) is the electron-phonon coupling constant.

When an impurity is added, the alloy is still a BCS superconductor, but with a modified coupling constant:

$$T_c = 1.13 \Theta_D e^{\frac{1}{g'}}$$

where the modified coupling constant is given by:

$$g' = g \left( \frac{1-Bx}{1+(Ag-B)x} \right)$$

The reduced superconducting transition temperature changes with impurity concentration \( x \) in a modified exponential form:

$$\frac{T_c}{T_{co}} = \exp \left( \frac{-Ax}{1-Bx} \right)$$

Where \( T_{co} \) is the transition temperature of the host matrix, \( x \) is the impurity concentration in atomic fraction and \( A \) and \( B \) are constants related to the density of states of the impurity atoms at the Fermi level \( N_i(E_F) \) and the effective Coulomb repulsion \( U_{eff} \) between the d-electrons with opposite spin.
In these equations, 2L+1 is the orbital degeneracy. The resulting curve of reduced transition temperature vs. x has a positive curvature in contrast to the paramagnetic impurity case. Kaiser's theory has been successfully applied to a number of systems\(^\text{79,80}\).

The superconducting transition temperature of all the samples in this investigation with transition metal substitution concentration x<10at.% were measured. The result for Cr, Co, Ni, and Ru substitutions are listed in Table 5. The reduced transition temperatures \(T_c/T_{c0}\) are plotted in Figure 8 as a function of transition metal impurity concentrations. All of the curves in Figure 8 have positive curvatures. The initial decreasing rate \(-dT_c/dx\) is the greatest for Cr with a value of 7.6K/at.%, and the smallest for Ru of 1.4K/at.%. It is noticeable that cobalt, showing none of its magnetic tendencies, suppresses \(T_c\) much less rapidly than Cr and Ni, with \(dT_c/dx\) = 1.6K/at.%. This is about the same as Ru. The weak effect of these transition metal substitutions on \(T_c\) is in strong contrast to the Zn–Mn and Zn–Cr system given in reference 75. The data of \(T_c\) vs. x in Figure 8 are fit to equation (9). The fitting constants for each impurity are listed in Table 6.

The logarithms of the reduced transition temperatures for Cr, Co, Ni, and Ru are plotted in Figure 9 as the function of x. The error bars
represent the transition widths. The lines in the figure are the fitting results. It can be seen that the fittings are very good for low percentage concentration but deviate at high concentrations. The deviation for high percentage Co substitutions may be caused by the limit of the solubility of Co in the matrix Lu2Fe3Si5, since Lu2Co3Si5 has a different structure (monoclinic space group).

Kaiser's calculation is based on the assumption that the host matrix is a BCS superconductor. Although heat capacity data given in Ref. 53 for Lu2Fe3Si5 show that this compound is not strictly a BCS superconductor, we can still use Kaiser's theory to estimate \( N_1(E_F) \), \( U_{\text{eff}} \), and other constants of the system since the basic mechanism of superconductivity for this compound is not different from the BCS theory.

The derived parameters for the system Lu2(Fe1-xTx)Si5 are listed in Table 7, where \( \Delta \) is the half width of the resonance state and \( E_d \) is the energy of the center of the resonance state measured from the Fermi level. The constants \( N(E_F) \) and \( g \) are calculated from the heat capacity measurement data given in Ref. 53. \( N_1(E_F) \) and \( U_{\text{eff}} \) are derived from equations (10) and (11) using the fitting constants. Other parameters are calculated from the following equations:

\[
\Delta = \frac{(2L+1)}{ \pi N_1(E_F)} \left[ 1+ \cot^2 \left( \frac{\pi \langle N \rangle}{2(2L+1)} \right) \right]^{-1} \quad (12)
\]

\[
E_d = \Delta \cot \left[ \frac{\pi \langle N \rangle}{2(2L+1)} \right] \quad (13)
\]

The resulting values are reasonable and comparable with those in the literature. The values of \( N_1(E_F) \) showed that the impurities have large densities of states. The half widths of the d-states are broad.
\(\Delta \gg k_BT_{\text{CO}}\), although they are smaller than the values predicted by Friedel\textsuperscript{82}. The values of \(U_{\text{eff}}\) are essentially equal to zero. This result shows that the coulomb repulsion which splits the cooper pairs is negligible. Equivalently, localized spin fluctuation are not present in any significant manner. From the curves of \(T_C\) vs. \(x\) and the fitting to Kaiser's theory we and conclude that Cr, Co, and Ni all behave like non-magnetic impurities. There is no localized magnetic moment formed at these impurity sites. The decrease of \(T_C\) is mainly caused by the pair weakening when the conduction electrons are scattered from a broad impurity state.

The data for Mn and Cu substitutions are plotted in Figure 10. The concentration percentages of Mn are not exact because some Mn evaporated during the arc-melting process. The exact mass loss of Mn is not known since the whole sample cracks and many small pieces fly out when cooling. However, from experience we estimate the loss to be less than 20\%. In contrast to other transition-metal substitutions, the curves of \(T_C\) vs. \(x\) have negative curvatures for Cu and Mn. The estimated critical concentrations at which the superconductivity will be destroyed completely are 2.5 and 2.75 at.% for Mn and Cu respectively. Compared with other systems with paramagnetic impurities such as ThGd, (ThGd)\textsubscript{Al}\textsubscript{2} (Ref. 77) and ZnMn, ZnCr (Ref. 75), the decreasing rate of \(T_C\) is still low. The linear dependence of \(T_C\) on \(x\) is not clear since we are working at relatively high concentrations (\(x \gg 1\) at.%).
Table 5. Superconducting transition temperatures of compounds

\[ \text{Lu}_2(\text{Fe}_{1-x}\text{T}_x)\text{Si}_5 \] (T=Cr,Mn,Co,Ni,Cu,Ru)

<table>
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<th>at.%</th>
<th>( T_c ) (K)</th>
<th>at.%</th>
<th>( T_c ) (K)</th>
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<td>2.30-1.82</td>
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<td>0.5Cr</td>
<td>3.38-3.10</td>
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<tr>
<td>1.0Cr</td>
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<td>1.0Ru</td>
<td>4.76-4.50</td>
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<td></td>
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<td>2.0Ru</td>
<td>3.65-3.45</td>
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<td>4.50-4.22</td>
<td>4.0Ru</td>
<td>2.41-2.07</td>
</tr>
<tr>
<td>1.7Co</td>
<td>3.75-3.15</td>
<td>6.0Ru</td>
<td>1.51-1.33</td>
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Table 6. The fitting constants for compounds Lu$_2$(Fe$_{1-x}$T$_x$)$_3$Si$_5$. Where T=Cr, Mn, Co, Ni, Ru

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<td>Ru</td>
<td>26.6</td>
<td>0.176</td>
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</table>

Table 7. The derived parameters

<table>
<thead>
<tr>
<th></th>
<th>$N_i(E_F)$$^a$</th>
<th>$U_{eff}$(eV)</th>
<th>$\Delta$(eV)</th>
<th>$E_d$(eV)</th>
<th>$\langle N \rangle$</th>
</tr>
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<tbody>
<tr>
<td>Cr</td>
<td>36.4</td>
<td>0</td>
<td>0.040</td>
<td>0.013</td>
<td>4</td>
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<td></td>
<td></td>
<td></td>
<td>0.043</td>
<td>0.000</td>
<td>5</td>
</tr>
<tr>
<td>Co</td>
<td>9.56</td>
<td>0.010</td>
<td>0.15</td>
<td>0.052</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.11</td>
<td>0.080</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.058</td>
<td>0.080</td>
<td>8</td>
</tr>
<tr>
<td>Ni</td>
<td>16.7</td>
<td>0</td>
<td>0.033</td>
<td>0.045</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.0091</td>
<td>0.028</td>
<td>9</td>
</tr>
<tr>
<td>Ru</td>
<td>7.90</td>
<td>0.004</td>
<td>0.18</td>
<td>0.062</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.13</td>
<td>0.094</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>0.069</td>
<td>0.095</td>
<td>8</td>
</tr>
</tbody>
</table>

$^a$The unit of $N_i(E_F)$ is states/eV-atom-spin.
Figure 8. Superconducting transition temperatures of compounds Lu$_2$(Fe$_{1-x}$T$_x$)$_3$Si$_5$ (T=Cr, Co, Ni, Ru). The lines are the guides for the eye.
Figure 9. The logarithm of reduced transition temperatures of compounds $\text{Lu}_2(\text{Fe}_{1-x}\text{T}_x)_3\text{Si}_5$ ($\text{T}=\text{Cr, Co, Ni, Ru}$). The lines are the fit.
Figure 10. Superconducting transition temperatures of compounds Lu$_2$(Fe$_{1-x}$Ti$_x$)$_3$Si$_5$. The lines are the guides for the eye.
According to the Abrikosov and Gor'kov's theory, the negative curvature means there are localized magnetic moments present at the impurity sites. It is not clear why among all the transition metal substitutions only Mn and Cu act as magnetic impurities. Are the magnetic moments located at the Mn and Cu site? Or is the moment induced on Fe site due to the replacement of some Fe by Mn or Cu? The location of the magnetic moment can be determined by Mössbauer studies. The electronic structures of Mn and Cu are somewhat special compared with other transition metals. Mn has an exactly half-filled d-shell and Cu has a filled d-shell. There may be some correlation between the electronic structure and the magnetization of Mn and Cu in these materials.

C. The Electrical Resistivity

The electrical resistivity of a material is mainly caused by the electron scattering off the lattice. Missing ions (defects), ions in wrong places (atomic disorder), or foreign atoms (impurities) all serve as scattering centers. The vibration of the lattice (phonons) causes electrons to be scattered too. For a simple model, the electrical resistivity can be written as the sum of two parts:

$$\rho(T) = \rho_{ph} + \rho_{im}$$

where $\rho_{ph}$ is the resistivity due to lattice vibration and $\rho_{im}$ is the contribution of crystal defects and impurities.

$\rho_{ph}$ is related to the kinetic energy of the lattice, so it decreases as the temperature is lowered. When the temperature of the
material is very low, \( \rho_{im} \) becomes the dominant part in the total electrical resistivity. It is called the residual resistivity.

Based on the Debye approximation for the phonon spectrum, Bloch-Grüneisen's s-s intraband scattering model predicted a \( T^5 \) dependence of \( \rho(T) \) for a simple metal at temperatures well below Debye temperature. Considering s-d interband scattering, Wilson showed that \( \rho(T) \) follows a \( T^3 \) law at low temperatures. Both models give a linear \( T \) dependence at high temperatures. These functional forms of the temperature dependence are observed in many metals. However, for some high \( T_c \) A15 compounds and some ternary superconducting compounds, the electrical resistivity differs noticeably from the \( T^5 \) and \( T^3 \) laws. The samples in this investigation showed unusual resistivity behavior too.

The electrical resistivity of the sample Lu\(_2\)Fe\(_3\)Si\(_5\) and two samples contain 4 at.% and 8 at.% Co were measured. The result \( \rho(T)/\rho(300K) \) is plotted in Figure 11. Table 8 lists the values of the residual resistivity, \( \rho \) at 300K and \( \rho_{300K}/\rho_{res} \) for the three samples. The

<table>
<thead>
<tr>
<th>x at.%</th>
<th>( \rho_{res} (\mu \Omega \text{ cm}) )</th>
<th>( \rho_{300K} (\mu \Omega \text{ cm}) )</th>
<th>( \rho_{300K}/\rho_{res} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>10.5</td>
<td>592.1</td>
<td>56.5</td>
</tr>
<tr>
<td>4.0</td>
<td>915.0</td>
<td>3164.6</td>
<td>3.46</td>
</tr>
<tr>
<td>8.0</td>
<td>1242.6</td>
<td>2773.9</td>
<td>2.23</td>
</tr>
</tbody>
</table>
residual resistivity ratios of samples with 4 at.% and 8 at.% Co were lower than that of the "pure" Lu$_2$Fe$_3$Si$_5$ as expected. One immediately notices that the values of $\rho$ for Co-containing samples are very high. These high values of $\rho$ are mostly attributed to the small cracks inside the samples formed during the sample synthesis.

Figure 12 is the bilogarithmic plot of $\rho(T) / \rho_{res}$ versus temperature. It shows that for most of the temperatures $\rho(T)$ does not have a simple power law dependence on temperature. However, for the sample Lu$_2$Fe$_3$Si$_5$, $\rho(T)$ varies approximately as $T^2$ at temperatures below 50K. For temperatures above 100K, $\rho(T)$ has a tendency to saturate. Instead of increasing linearly with $T$, $\rho(T)$ is proportional to $\log T$.

The electrical resistivities of the compounds containing Co deviate from the $T^2$ law at low temperatures and tend to be linear in $T$ at high temperatures. This is probably because when the impurity concentration is high, the simple additive resistivity model is not applicable anymore.

The $T^2$ behavior has been observed in other compounds such as Nb$_3$Sn, Nb$_3$Al (Ref. 88) and Y$_5$O$_4$Ge$_{10}$ (Ref. 87) and some non-magnetic transition metals too. It was qualitatively explained by Rice$^{89}$ and Webb et al.$^{88}$ on the basis of electron-electron scattering and electron-phonon scattering. Quantitative calculations were done by Rice on electron-electron scattering for some non-magnetic transition metals and by Webb et al. on electron-phonon scattering for the high $T_c$ A15 compounds. For our compounds, the observed $T^2$ term was three orders of magnitude larger than has been observed in transition metals and one order of magnitude larger than in A15 compounds.
Figure 11. Reduced electrical resistivity of Lu$_2$Fe$_3$Si$_5$ and the Co-containing compounds.
Figure 12. Bilogarithmic plot of resistivity vs. temperature
There is a variety of theories which attempt to explain the saturation of $\rho(T)$ at high temperatures. Among them are a s-d band overlying model by Cohen, Cody and Halloran\textsuperscript{90}, and a lattice vibrational mode hardening model by Allen et al.\textsuperscript{91}, Z. Fisk and G. W. Webb\textsuperscript{92} interpreted the phenomenon of saturation as due to the attainment of the lower limit of the electron mean free path in the solid which they took to be on the order of one interatomic distance. This limit gives the electrical resistivity a "saturation value" when the temperature is well above the Debye temperature. For our samples, the Debye temperature is so high (485K) that it is out of the upper measurement limit of our instrument. Therefore, the saturation value $\rho_{Sat}$ could not be determined.

From the resistivity and other data taken for the compound Lu$_2$Fe$_3$Si$_5$, we could say that a quantitative explanation for the resistivity behavior is not possible. A combination of complex scattering mechanism must be responsible for the unusual $T$ dependence of $\rho$. A complete understanding of the phonon spectrum and the energy bands are necessary to interpret the behavior of electrical resistivity of these pseudo-ternary compounds.

D. The Static Magnetic Susceptibility

The magnetic susceptibility is a very important quantity since it represents the response of a material to an applied magnetic field. The magnetic susceptibility is defined as:
where $M$ is the magnetization, and $H$ is the applied magnetic field intensity. If the magnetic susceptibility of a substance is positive, the substance is paramagnetic, and if $\chi$ is negative, the substance is diamagnetic. The magnetic moment of an atom arises mainly from three sources. The electron spin and the orbital angular momentum of the electrons about the nucleus give a paramagnetic contribution. While the change in the orbital momentum induced by an applied magnetic field gives a diamagnetic contribution. If a substance has an ordered array of spins and a magnetic moment below a certain temperature even in the absence of a magnetic field, the substance is said to order magnetically. Magnetically ordered materials can be classified roughly into ferromagnet, antiferromagnet, or ferrimagnet according to the ordered arrangement of spins.

Atoms with the electronic shells all filled are usually diamagnetic. The magnetic susceptibility of such a material is called the Larmor diamagnetic susceptibility which is independent of temperature. If an atom has unfilled electronic shells, a paramagnetic correction has to be added to the Larmor diamagnetic susceptibility. When the sum of the spin and the orbital angular momentum $J$ is zero, this paramagnetic term is independent of temperature. If $J$ is not zero, the paramagnetic susceptibility varies inversely with temperature:

$$\chi = \frac{C}{T} \quad (15)$$

$$C = \frac{N u_{\text{eff}}^2}{3 k_B} \quad (16)$$
This is known as Curie's Law and $C$ is the Curie constant. $\mu_{\text{eff}}$ is the effective magneton, $k_B$ is the Boltzmann constant, and $N$ is the number of atoms.

In a metal, the coupling of the intrinsic spin of the conduction electrons with the applied field and the coupling of the orbital motion of the conduction electrons with the applied field have to be considered. These two effects give the Pauli spin paramagnetic susceptibility and the Landau diamagnetic susceptibility.

To describe the magnetic behavior of a magnetically ordered substance, Pierre Weiss assumed that there is an exchange field proportional to the magnetization created by the lining up of the spins. In this model, the applied field can be replaced by an effective magnetic field $H_{\text{eff}}$. By using this effective field, the obtained magnetic susceptibility above the magnetic ordering temperature has a temperature dependence in a form:

$$\chi = \frac{C}{T - \Theta}$$

This is known as the Curie-Weiss law. $\Theta$ is the magnetic ordering temperature. If the substance is ferromagnetically ordered, $\Theta$ is positive and called the Curie temperature. If the substance is antiferromagnetically ordered, $\Theta$ is negative and called the Néel temperature. Although the assumption P. Weiss made is very simple, the magnetic susceptibilities of many materials are found to follow this law very well. However, the temperature dependence of $\chi$ is not always so simple. $\chi$ is related to the Fermi energy and the density of states at the Fermi level; two quantities that vary with temperature. As a
result, the $T$ dependence of the magnetic susceptibility of some metals and a number of compounds cannot be described by a simple equation such as the Curie-Weiss law. Lu$_2$Fe$_3$Si$_5$ is one of many examples.

The static magnetic susceptibilities of all the samples of the compounds Lu$_2$(Fe$_{1-x}$Tx)$_3$Si$_5$ were measured. The measured result for Lu$_2$Fe$_3$Si$_5$ is shown in Figure 13. It is in good agreement with previous data given in ref. 53. The temperature dependence of $\chi$ does not follow a Curie-Weiss law. The value of $\chi$ rather increases slightly as temperature increases with values at 35K and 300K of $2.07 \times 10^{-4}$ and $3.77 \times 10^{-4}$ emu/mole respectively. At temperatures below 35K, $\chi$ increases with decreasing temperature. A minimum point is thus attained at a temperature around 35K. The increasing rate of $\chi(T)$ is the greatest in the temperature range between 100 and 200K, and slows down at higher temperatures. $\chi(T)$ has a tendency to saturate at high temperatures.

The small upswing at the low temperature end in $\chi(T)$ is believed due to the small amount of free iron in Lu. The estimated amount of free iron in the sample Lu$_2$Fe$_3$Si$_5$ is less than 180 ppm.

As other transition metals are added into this compound, the magnetic susceptibility changes. Figures 14 and 15 show the measured magnetic susceptibilities for compounds with 2% Fe replaced by other transition metals. When a small amount of Ru or Cu is substituted for Fe, the change in the magnetic susceptibility is small. The small upswing and the $T$ dependence remain unchanged, keeping the overall shapes of the curves similar. At any given temperature, the value of $\chi$ is slightly lower for the doped sample. Figure 16 shows the effect of Ru substitution on $\chi(T)$. As is seen, Ru substitution lowers the value
of $\chi$. As the Ru concentration increases, the minimum point moves slowly to the right, while the $T$ dependence of $\chi(T)$ is almost unchanged. When Fe is completely replaced by Ru, the compound Lu$_2$Ru$_3$Si$_5$ becomes diamagnetic at all temperatures in the measuring range. There is still a small upswing at the low temperature end attributed to a small amount of paramagnetic impurities in the sample, and $\chi(T)$ increases with the increasing temperature at $T > 75K$. The values of $\chi$ at 75K and 300K are $-2.20 \times 10^{-4}$ emu/mole and $-1.88 \times 10^{-4}$ emu/mole respectively. From the curves in Figure 16 one can see that there must be some Ru concentration which makes the crossover from paramagnetic to diamagnetic.

In contrast to Ru and Cu, when nominally magnetic transition metals such as Cr, Mn, Co, and Ni replace Fe, the small upturn at the low temperature end becomes more pronounced. Compared with the value of $\chi(T)$ for the "pure" compound, the values of $\chi$ at low temperature are higher, and the minimum point moves to the right. $\chi(T)$ increases more slowly at high temperatures, while the value of $\chi(T)$ at the high temperature end remains almost unchanged. The $\chi(T)$ curve therefore becomes more Curie-Weiss like, especially at low temperatures.

If we concentrate on the Co substitution (Figure 17), we can see that the value of $\chi(T)$ at the low temperature end increases as the Co concentration increases. As more Fe is substituted by Co, $\chi(T)$ becomes more and more Curie-Weiss like. When Fe is completely replaced by Co, $\chi(T)$ can be fit very well by a Curie-Weiss equation (Figure 18).

In order to see more clearly the effect of magnetic transition-metals on the magnetic susceptibility, $\chi(T)$ of the compound Lu$_2$Fe$_3$Si$_5$ was subtracted from the $\chi(T)$ of compounds Lu$_2$($Fe_{1-x}T_x$)$_3$Si$_5$ (where $T$= Cr, Mn, Ni, Co), the differences were fit to the equation:
\[ X(T) = X_0 + \frac{C}{T - \Theta} \]  

where \( X_0 \) is the temperature independent part of the susceptibility including the Larmor diamagnetism, Pauli paramagnetism and Landau diamagnetism. \( C \) is the Curie constant, and \( \Theta \) is the magnetic ordering temperature. The results of these fits are given in Table 9. It was found that the susceptibility difference for Mn-containing compounds fits the equation surprisingly well over the whole measured temperature range (see Figure 19). The susceptibilities of samples containing Ni and Cr fit the equation well only at low temperatures (Figures 20, 21). Compared with other transition metal substitutions, Co gives rather poor fits even at high concentrations (Figures 22, 23).

The effective paramagnetic moments \( \mu_{\text{eff}} \) are calculated from the fitting constant \( C \):

\[
C = \frac{N_A \mu_{\text{eff}}^2}{3 k_B} = \frac{N_A \mu_B^2}{3 k_B},
\]

where \( \mu \) is the effective Bohr magneton number, \( \mu_B \) is the Bohr magneton, \( k_B \) is the Boltzmann constant, and \( N_A \) is the Avogadro’s number. As can be seen, the value of \( \mu \) for each transition-metal element is smaller than the measured value of \( \mu \) for the corresponding ion. This is attributed to the effect of the crystalline electric field surrounding the transition metal atoms in the compound.

The fit to the Curie-Weiss equation of the magnetic susceptibility of Mn-containing samples gives strong support to the assumption from the variation of superconducting critical temperature that Mn forms a localized magnetic moment in the compound \( \text{Lu}_2(\text{Fe}_{1-x}\text{Mn}_x)_3\text{Si}_5 \). The fact
Table 9. The fitting constants of the difference in magnetic susceptibilities of compounds Lu$_2$(Fe$_{1-x}$T$_x$)$_3$Si$_5$ and the compound Lu$_2$Fe$_3$Si$_5$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\chi_0$ [10$^{-5}$ emu/mole]</th>
<th>$C$ [10$^{-3}$ K-emu/mole]</th>
<th>$p^a$ [K]</th>
<th>$\Theta$ [K]</th>
<th>fit range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr 2%</td>
<td>4.95±0.50</td>
<td>9.3±0.6</td>
<td>1.10±0.29</td>
<td>-18.0±1.5</td>
<td>0 - 100</td>
</tr>
<tr>
<td>Mn 2%</td>
<td>2.24±0.11</td>
<td>1.30±0.01</td>
<td>1.31±0.12</td>
<td>-3.24±0.14</td>
<td>0 - 300</td>
</tr>
<tr>
<td>Ni 2%</td>
<td>-2.63±0.12</td>
<td>2.11±0.07</td>
<td>0.53±0.08</td>
<td>1.23±0.21</td>
<td>0 - 75</td>
</tr>
<tr>
<td>Co 10%</td>
<td>1.37±0.35</td>
<td>1.81±0.18</td>
<td>0.22±0.07</td>
<td>-16.2±1.85</td>
<td>0 - 50</td>
</tr>
<tr>
<td>Co 35%</td>
<td>-9.93±5.76</td>
<td>50.0±6.1</td>
<td>0.61±0.22</td>
<td>-29.6±12.1</td>
<td>0 - 240</td>
</tr>
<tr>
<td>Co 100%</td>
<td>-18.6±4.5</td>
<td>280±20</td>
<td>0.87±0.24</td>
<td>-110.5±6.5</td>
<td>0 - 300</td>
</tr>
</tbody>
</table>

$^a$ $p$ is the effective Bohr magneton number per transition-metal atom.
that the magnetic susceptibility of the Ni- and Cr- containing samples fits the Curie-Weiss equation only at low temperatures indicates that Cr and Ni do not have localized magnetic moment in the compound. The poor fits of $\chi(T)$ for the Co-containing samples together with the unusually weak effect of Co on the superconducting transition temperature show that Co behaves differently from other transition-metals in the compound Lu$_2$Fe$_3$Si$_5$. The reasons for this peculiar behavior are not clear.

An increase in $\chi(T)$ with increasing temperature has been observed in some transition metals$^{95}$, in $\alpha$-Ce (Ref. 96), in superconducting ternary compounds TlMo$_6$S$_8$ (Ref. 97), Y$_5$Rh$_4$Ge$_{10}$ (Ref. 68), and in CeSn$_3$ (Ref. 98). Different explanations were applied to these systems, for example: (i) charge density wave formation (for Y$_5$Rh$_4$Ge$_{10}$); (ii) spin density wave formation (for CeSn$_3$); (iii) electron-phonon interaction (for Cr and Rh); (iv) structural phase transition (for TlMo$_6$S$_8$); (v) the shape of the curve of the electronic density of states at the Fermi level in the 3-d band (for the transition metals).

The first two explanations could not be applied to the Lu$_2$Fe$_3$Si$_5$ system since there is no anomalous peak observed in the electrical resistivity measurement, also the heat capacity fit$^{99}$ has no term of the form $D T^3 \ln T$ for this compound. The third explanation was offered by D. J. Kim$^{100}$ who calculated the temperature dependence of magnetic susceptibility of several kind of systems considering the electron-phonon interaction effect. According to this theory, when the electron-phonon interaction is constructive, the magnetic susceptibility will increase with increasing temperature. $\chi(T)$ can be fit into an equation:
\[ X(T) = \frac{C}{T_a - T} \]  

where \( C \) and \( T_a \) are constants. The magnetic susceptibility of Cr and Rh can be fit to this equation very well; however, our data of \( X(T) \) for the host compound \( \text{Lu}_2\text{Fe}_3\text{Si}_5 \) cannot be fit by this equation. We conclude that for this family of compounds, the electron-phonon interaction is not the major cause for the increasing \( X(T) \). This leaves explanations (iv) and (v) to consider. Low temperature x-ray diffraction needs to be done on the compound \( \text{Lu}_2\text{Fe}_3\text{Si}_5 \) to see whether there is any structural phase transition at low temperatures. Although we have seen that the temperature dependences of \( X(T) \) for the compounds \( \text{Lu}_2\text{Fe}_3\text{Si}_5 \) and \( \text{Lu}_2\text{Co}_3\text{Si}_5 \) are different, additional samples of \( \text{Lu}_2T_3\text{Si}_5 \) (where \( T \) = transition metals) may be synthesized in order to see whether \( X(T) \) is related to shape of the density of states in the 3-d band. The behavior of the magnetic susceptibility of the compound \( \text{Lu}_2\text{Fe}_3\text{Si}_5 \) is probably attributed to some anomalies in the density of states at the Fermi level. Band structure calculations could be of great assistance and necessary for a quantitative explanation for the \( T \) dependence of the magnetic susceptibility of these compounds.

E. Low Temperature Specific Heat

The low temperature heat capacity measurement is an useful experimental tool in studying the physical properties of a material. It provides information on the lattice vibrations, electronic states, energy band structure, magnetic ordering, spin density waves, and more.
Figure 13. The magnetic susceptibility of $\text{Lu}_2\text{Fe}_3\text{Si}_5$
Figure 14. The magnetic susceptibilities of Lu$_2$Fe$_3$Si$_5$ and the 2% Cr-, Mn-, Ni-containing samples.
Figure 15. The magnetic susceptibilities of $\text{Lu}_2\text{Fe}_3\text{Si}_5$ and the 2% Co-, Cu-, Ru-containing samples
Figure 16. The magnetic susceptibilities of compounds Lu$_2$(Fe$_{1-x}$Ru$_x$)$_3$Si$_5$. filled circle: x=0; cross: x=0.10; X: x=0.25; circle: x=0.35 square: x=1.0
Figure 17. The magnetic susceptibilities of compounds Lu$_2$Fe$_{1-x}$Co$_x$)$_3$Si$_5$
Figure 18. The magnetic susceptibility of Lu$_2$Co$_3$Si$_5$ fit to a Curie-Weiss equation.
Figure 19. $X_{\text{Mn}}$ difference fit to Curie-Weiss Equation
Figure 20. $\chi (\text{Ni})$ difference fit to Curie-Weiss Equation
Figure 21. $\chi$ (Cr) difference fit to Curie-Weiss Equation
Figure 22. $\chi(10\%\text{Co})$ difference fit to Curie-Weiss Equation
Figure 23. $\chi_{(35\%\text{Co})}$ difference fit to Curie-Weiss Equation

Lu$_2$(Fe$_{65}$ Co$_{35}$)$_3$Si$_5$
In the study of superconductivity, the low temperature heat capacity measurement is crucial in confirming the bulk nature of a superconductor.

In 1907, Einstein first applied the quantization of the vibrational energy of atoms in a crystal lattice, and calculated the lattice contribution to the specific heat on a simple assumption that all the atoms vibrate at the same frequency. Based on Einstein's approach, Debye calculated the lattice specific heat by using a linear dispersion relation for lattice vibrations. According to Debye's model, the specific heat attributed to the lattice vibration is given by:

\[
C = \frac{12 \pi^4}{5} N_A r k_B \left( \frac{T}{\Theta_D} \right)^3 = \beta T^3
\]  

(21)

\[
\beta = \frac{12 \pi^4 N_A r k_B}{5 \Theta_D^3}
\]  

(22)

In these equations, \(N_A\) is the Avogadro's number, \(r\) is the number of atoms in a molecule, \(\Theta_D\) is the Debye temperature which is a measure of the temperature above which all the lattice vibrations begin to be excited, and below which only the low frequency mode is excited. This result turned out to be a successful explanation for the thermal behavior of many solids.

The electronic contribution to the specific heat can be calculated based upon the assumption that conduction electrons at low temperatures obey Fermi-Dirac statistics. The resulting specific heat \(C_e\) attributed to the motion of conduction electrons in a metal is given by:

\[
C_e = \frac{2}{3} k_B^2 N(E_F) T = \gamma T
\]  

(23)
where \[ \gamma = \frac{\pi^2}{3} k_B^2 N(E_F) \] (24)

In these equations, \( k_B \) is the Boltzmann constant and \( N(E_F) \) is the electronic density of states per spin at the Fermi surface.

For a simple normal metal, the heat capacity is often written as the sum of the lattice contribution and the electronic contribution:

\[ C = \gamma T + \beta T^3 + \alpha T^5 \] (25)

The first two terms in this equation are the electron and phonon contributions mentioned above, the third term arises from the anharmonicity of the lattice. At room temperature, the electronic contribution is negligible compared with the lattice contribution. When the temperature is low, the electronic contribution is a major portion of the total heat capacity.

For a superconductor, at the transition temperature \( T_C \), the heat capacity is not continuous. There is a jump between the superconducting state heat capacity \( C_S \) and the normal state heat capacity \( C_n \) at \( T_C \). The BCS theory predicted that at \( T_C \), the value of \( (C_S - C_n)/\gamma_n T_C \) is 1.43.

Above \( T_C \), the heat capacity is the same as in a normal metal, below \( T_C \), the heat capacity due to the electrons' superconduction is found to vary with temperature as \( C_{es} \propto \exp(-\Delta/T) \), where \( \Delta \) is the half width of the energy gap which separates the excited energy level from the ground state.

If spin fluctuations are present in the sample, then in the equation describing the total heat capacity there will be an extra term proportional to \( \propto T^3 \ln T \).
Many other factors affect the total heat capacity of a substance, each having a different temperature dependence. Fortunately, under certain condition, only a few of them make significant contributions. Therefore, fitting the measured heat capacity to a certain kind of equation will help one to understand the mechanism of the physical behavior of a substance.

The low temperature heat capacity of the compound \( \text{Lu}_2\text{Fe}_3\text{Si}_5 \) was measured by C. B. Vining\(^5^3\). He reported that in the temperature range from \( T_c (6.1\text{K}) \) to 18K, the total heat capacity of this compound can be described by Eq. (25) with a large \( T^5 \) term. At \( T_c \), the jump between \( C_s \) and \( C_n \), \( \Delta C / \gamma_n T_c \) has a value of 0.99 which is much smaller than predicted by the BCS theory. Below \( T_c \), the heat capacity is remarkably simple, it can be described by \( C_s = \gamma_s T + \beta_s T^3 \).

The heat capacities of the samples with 1 at.\% Co, 4 at.\% Co, 1 at.\% Ru and 6 at.\% Ru were measured in a temperature range from 0.5K to 30K. The data are shown in Figures 24 through 31. For each sample, both the \( C \) vs. \( T \) and \( C/T \) vs. \( T^2 \) plot are presented, and the detailed variations of the heat capacity \( C \) and \( C/T \) around \( T_c \) are presented in the inset of each graph.

The normal state heat capacity data of each sample was fit by Eq. (25) in the temperature range from \( T_c \) to 20K. The fits are reasonably good for the samples with 1 at.\% Co or Ru substitution, but rather poor for the two samples with higher Co or Ru concentration. For the latter two samples, the heat capacity data in the temperature range from 1.5K to 6K have large deviations from the values calculated by the least square fits to Eq. (25) resulting in a total root-mean-square (rms)
deviation of 9% and 21% for the 6 at.% Ru and 4 at.% Co sample respectively. The fitting constants and the derived parameters from the least square fit are listed in Table 10. For each sample, the electron-phonon coupling constant \( \lambda \) is calculated from the McMillan equation\(^{19}\):

\[
\lambda = \frac{1.04 + \mu^* \ln \left( \frac{\Theta_D}{1.45 T_c} \right)}{(1-0.62\mu^*) \ln \left( \frac{\Theta_D}{1.45 T_c} \right) - 1.04}
\]

by using \( \mu^* = 0.1 \).

Compared with the "pure" \( \text{Lu}_2\text{Fe}_3\text{Si}_5 \) compound, \( \gamma_n \) decreases and \( \beta_n \) increases as the Co and Ru concentration increases. These changes result in a decrease in both the Debye temperature and the the electronic density of states at the Fermi level. The lattice contribution term \( \beta_n T^3 + \alpha_n T^5 \) to the total heat capacity at \( T_c \) is about 20% for the samples with 1 at.% Co or Ru substitution. This is similar to the "pure" \( \text{Lu}_2\text{Fe}_3\text{Si}_5 \) compound. In contrast, the lattice contribution is much smaller for the other two samples because of the low \( T_c \) value. In each case, at \( T = 10K \), the \( T^5 \) term contributes about 13% to the total heat capacity, indicating the complex phonon spectrum of these compounds.

Below \( T_c \), we attempted to fit the superconducting state heat capacity data to \( \beta_s T^3 + e^{-b/T} \). The fits were not good with a rather large deviation. The values of \( \beta_s \) from the fit were an order larger in magnitude than \( \beta_n \), and the values of \( a \) and \( b \) are physically unrealistic. The fit value lies below the data at very low temperatures. Instead, the data are fit to \( C_s = \gamma_s T + \beta_s T^3 \) with fitting errors from 1.5% to
3.6%. The values of $\beta_2$ in this fit are an order of magnitude larger than $\beta_n$. The values of $\gamma_1$ and $\beta_2$ are both increased compared with the "pure" compound. The large linear term contribution to the heat capacity in the superconducting state is explained by Vining et al. as a part of the energy band remaining normal below $T_c$ which is weakly coupled with the superconducting band$^{53}$. There is a possibility that when the impurity is added, the fraction of the normal electrons is enhanced.

It is noticeable in Table 10 that the values of $\Delta C/\gamma_n T_c$ for the compounds Lu$_2$(Fe$_{1-x}$Ti$_x$)$_3$Si$_5$ are much smaller than the BCS value of 1.43, showing that these ternary compounds are not BCS superconductors. The normalized heat capacity jump $\Delta C/\Delta C_0$ at $T_c$ vs. $\Delta T_c/\Delta T_{so}$ is plotted in Figure 32. Obviously it deviates from the BCS prediction considerably. The dot dashed line in the figure is from the theory of Abrikosov and Gor'kov. Apparently, $\Delta C/\Delta C_0$ does not follow this line either. A similar characteristic depression of $\Delta C/\Delta C_0$ is observed in other matrix-impurity systems$^{101-105}$. Some of these systems show a Kondo effect in the electrical resistivity measurement; however, there is no minimum point observed in our resistivity data.

The deviation of the normal state heat capacity data from the Debye model is reported for other superconducting ternary compounds$^{106,107}$. It is generally believed that the reason for the deviation is the complex phonon spectrum of these ternary compounds. Substituting part of the Fe by other transition metals in the compound Lu$_2$Fe$_3$Si$_5$ would make the phonon spectrum more complicated. This is most probably why our heat capacity data for high concentration Co and Ru cannot be described adequately by a simple Debye model.
Table 10. The fitting constants and the derived parameters for the heat capacity data of Lu$_2$(Fe$_{1-x}$T$_x$)$_3$Si$_5$ compounds (T = Co and Ru)

<table>
<thead>
<tr>
<th></th>
<th>Lu$_2$Fe$_3$Si$_5^a$</th>
<th>1 at.%Co</th>
<th>4 at.%Co</th>
<th>1 at.%Ru</th>
<th>6 at.%Ru</th>
</tr>
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<tbody>
<tr>
<td>$T_c$ (K)</td>
<td>6.10</td>
<td>4.37</td>
<td>1.36</td>
<td>4.64</td>
<td>1.24</td>
</tr>
<tr>
<td>$\gamma_n$ (mJ/mole-K$^2$)</td>
<td>27.8</td>
<td>21.1</td>
<td>15.7</td>
<td>19.9</td>
<td>15.9</td>
</tr>
<tr>
<td>$\beta_n$ (mJ/mole-k$^4$)</td>
<td>0.170</td>
<td>0.257</td>
<td>0.340</td>
<td>0.251</td>
<td>0.242</td>
</tr>
<tr>
<td>$\alpha_n$ (mJ/mole-K$^6$)</td>
<td>7.97x10$^{-4}$</td>
<td>6.36x10$^{-4}$</td>
<td>2.65x10$^{-4}$</td>
<td>6.55x10$^{-4}$</td>
<td>6.30x10$^{-4}$</td>
</tr>
<tr>
<td>fit rms $\Delta%$</td>
<td>1%</td>
<td>3.3%</td>
<td>21%</td>
<td>2.0%</td>
<td>8.9%</td>
</tr>
<tr>
<td>$\Delta C/\gamma_n T_c$</td>
<td>0.99</td>
<td>0.56</td>
<td>0.45</td>
<td>0.66</td>
<td>0.44</td>
</tr>
<tr>
<td>$\Delta T(K)$</td>
<td>0.3</td>
<td>0.46</td>
<td>0.24</td>
<td>0.27</td>
<td>0.19</td>
</tr>
<tr>
<td>$\gamma_S$ (mJ/mole-K$^2$)</td>
<td>10.14</td>
<td>16.21</td>
<td>25.43</td>
<td>13.39</td>
<td>24.20</td>
</tr>
<tr>
<td>$\beta_S$ (mJ/mole-K$^4$)</td>
<td>1.346</td>
<td>1.54</td>
<td>8.57</td>
<td>1.44</td>
<td>4.89</td>
</tr>
<tr>
<td>fit rms $\Delta%$</td>
<td>0.7%</td>
<td>2.4%</td>
<td>3.4%</td>
<td>3.6%</td>
<td>1.5%</td>
</tr>
<tr>
<td>$\Theta D(K)$</td>
<td>485</td>
<td>423</td>
<td>385</td>
<td>426</td>
<td>432</td>
</tr>
<tr>
<td>$N(E_F)$ (sts./eV-atom-spin)</td>
<td>0.59</td>
<td>0.45</td>
<td>0.33</td>
<td>0.42</td>
<td>0.34</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.51</td>
<td>0.50</td>
<td>0.40</td>
<td>0.51</td>
<td>0.39</td>
</tr>
</tbody>
</table>

$^a$Data for this compound are taken from Ref.53.
Figure 24. Specific heat of Lu$_2$(Fe$_{99}$Ru$_{01}$)$_3$Si$_5$. The inset is the detailed change around $T_c$. 
Figure 25. Specific heat $C/T$ vs. $T^2$ for Lu$_2$(Fe$_{0.99}$Ru$_{0.01}$)$_3$Si$_5$. The inset is the detailed change around $T_c$. 
Figure 26. Specific heat of $\text{Lu}_2(\text{Fe}_{0.94}\text{Ru}_{0.06})_3\text{Si}_5$. The inset is the detailed change around $T_C$. 

$C \text{ (mJ/mole-K)}$ vs $T \text{ (K)}$.
Figure 27. Specific heat $C/T$ vs. $T^2$ for $\text{Lu}_2(\text{Fe}_{0.94}\text{Ru}_{0.06})_3\text{Si}_5$. The inset is the detailed change around $T_C$. 
Figure 28. Specific heat of Lu$_2$(Fe$_{99}$Co$_{0.01}$)$_3$Si$_5$. The inset is the detailed change around $T_C$. 
Figure 29. Specific heat $C/T$ vs. $T^2$ for Lu$_2$(Fe$_{0.99}$Co$_{0.01}$)$_3$Si$_5$. The inset is the detailed change around $T_c$. 

Lu$_2$(Fe$_{0.99}$Co$_{0.01}$)$_3$Si$_5$
Figure 30. Specific heat of Lu$_2$(Fe$_{0.96}$Co$_{0.04}$)$_3$Si$_5$. The inset is the detailed change around $T_c$. 
Figure 31. Specific heat $C/T$ vs. $T^2$ for $\text{Lu}_2(\text{Fe}_{.96}\text{Co}_{.04})_3\text{Si}_5$. The inset is the detailed change around $T_c$. 
Figure 32 Reduced specific jump at $T_c$ vs. reduced transition temperature
A polynomial with higher powers of $T$ (up to $T^9$) was applied to fit the normal state heat capacity data. The fit is good with a rms deviation of 1%. This better fit is to be expected since we are using more fitting parameters. We reject this method for analysis purposes since the additional terms provide no physical insight into the problem. Exploring another alternative, we note that there is no sign that our heat capacity data can be fit to:

$$\frac{C}{T} = A + B T^2 + D T^2 \ln T,$$

(7)

a characteristic heat capacity when spin fluctuation are present. Therefore, spin fluctuations are not the cause of the depression of $T_C$ and the anomalous temperature dependence of the magnetic susceptibility of these compounds.

From the heat capacity data for the samples containing Co and Ru, one can see that the effect of Co and Ru substitutions on the heat capacity of the compound Lu$_2$Fe$_3$Si$_5$ are very similar. This result is in agreement with our superconducting $T_C$ measurement.
IV. CONCLUSION AND SUMMARY

The measurements of the superconducting and normal state properties of compounds Lu$_2$(Fe$_{1-x}$T$_x$)$_3$Si$_5$ are reported. Here T=Cr, Mn, Co, Ni, Cu and Ru; x<0.02 for Cr, Mn, Ni, and Cu, while for Co and Ru, x ranges from 0.01 to 1.0.

When less than 2 at.% Fe is substituted by other transition metals, the changes in the lattice parameters are very small. When the concentration of the substituted transition metals increases, the changes in the lattice parameters obey Vegard’s law. The lattice constants a and c and the unit cell volume have a linear dependence on x across the whole Ru series, while the deviation from linearity for the Co series when x is greater than 0.10, is obviously due to the presence of the second phase Lu$_2$Co$_3$Si$_5$.

The detailed variation of the superconducting transition temperature $T_C$ as a function of impurity concentration was measured. The reduced transition temperature $T_c/T_{CO}$ was fit to Kaiser’s equation. A good agreement with Kaiser’s theory was obtained for Cr, Co, Ni, and Ru. The effect of Co substitution on $T_C$ is weaker than that of other 3d transition metals, but similar to Ru. The compound remains superconducting ($T_C=0.49K$) even when 10 at.% Co is substituted for Fe. The decrease of $T_C$ for these transition metal substitutions is more rapid than that for ordinary non-magnetic impurities but less rapid than for paramagnetic impurities. The derived parameters from the fitting constants showed that the impurity state is broad with a high density of
states at the Fermi level. The effective Coulomb repulsion between the d electrons is very small or possibly zero. We conclude that the transition metals Cr, Co, Ni, and Ru form no localized magnetic moment in the compounds Lu$_2$(Fe$_{1-x}$T$_x$)$_3$Si$_5$. The depression of $T_C$ is caused by the scattering of conduction electrons off the broadened impurity site. In contrast, the variations of $T_C$ for Mn and Cu substitutions show negative curvatures as predicted by the Abrikosov and Gor'kov theory for paramagnetic impurities. This indicates the presence of localized magnetic moments. The localized magnetic moments in the Mn- and Cu-containing samples are probably induced by these impurities on the Fe site. The reasons for the different magnetic behavior of these transition metals are not clear. Noticing the strong covalent bonding between Fe atoms and their nearest Si neighbors, we suspect that Mn with an exactly half-filled 3d-shell and Cu with a completely filled 3d-shell may change the nature of these covalent dependent bonds, resulting in localized electrons to develop magnetic moments. More experiments such as Mössbauer studies, low temperature x-ray diffraction and measurement of the change in lattice parameters for samples with higher Mn or Cu concentrations could be helpful to the understanding of the magnetic behavior of these transition metals in the host Lu$_2$Fe$_3$Si$_5$. Band structure calculations should give a realistic description of the character of the conduction electrons in these compounds and help to determine the locality of the electrons.

The static magnetic susceptibility of the compound Lu$_2$Fe$_3$Si$_5$ has a temperature dependence different from a Curie-Weiss expression. Instead, $\chi(T)$ increases slightly as temperature increases for $T>30$K.
The addition of the transition metals changes the temperature dependence of $\chi$. As the Cr, Ni, Mn, and Co substitution concentration increases, $\chi(T)$ becomes more Curie-Weiss like. There is no definite correlation between the changes in the magnetic susceptibility and the superconducting transition temperatures. The difference between $\chi(T)$ of the Cr-, Ni-, and especially the Mn-containing samples and $\chi(T)$ of the "pure" compound Lu$_2$Fe$_3$Si$_5$ can be fit to a Curie-Weiss equation, while for the Co- containing samples, this fit is rather poor. This experimental fact, together with the effect of Co and Mn substitutions on the superconducting transition temperature, leads us to conclude that Co behaves differently from the other 3d transition metals, while Mn forms localized magnetic moments in the compound Lu$_2$(Fe$_{1-x}$Mn$_x$)$_3$Si$_5$. Ru substitution lowers the value of $\chi(T)$, but keeps the overall shape unchanged. The magnetic susceptibility of the compound Lu$_2$Ru$_3$Si$_5$ is diamagnetic at all temperatures in the measuring range, while the magnetic susceptibility of the compound Lu$_2$Co$_3$Si$_5$ follows the Curie-Weiss law very well. It is obvious that the temperature dependence of the magnetic susceptibility is related to the properties of the transition metal in the compound Lu$_2$T$_3$Si$_5$ (T=transition metal). We conclude that the anomalous temperature dependence of $\chi(T)$ of the compound Lu$_2$Fe$_3$Si$_5$ is probably attributed to some anomalies in the density of states at the Fermi level while these anomalies are related to the electronic structure of the transition metals in this compounds.

The low temperature specific heat measurements on the compounds containing 1 at.% Co or Ru, 4 at.% Co and 6 at.% Ru showed that Co and Ru substitutions have similar effects on the specific heat of the
compound Lu$_2$Fe$_3$Si$_5$. The fitting of the heat capacity C(T) showed that the addition of Co or Ru lowers both the Debye temperature of the compound and the electronic density of states at the Fermi level. The fit of the superconducting state C(T) to the equation $\beta_s T^3 + a e^{-b/T}$ gives unphysical values of $a$ and $b$, while the good fit to the equation $\gamma_s T + \xi T^3$ and the increasing of $\gamma_s$ showed that below $T_C$ the normal fraction of electrons in the energy band is enhanced by the Co or Ru substitution. The fits of C(T) to the equations $\gamma_s T + \beta_s T^3$ below $T_C$ and $\gamma_n T + \beta_n T^3 + \sigma_n T^5$ above $T_C$ are not as good as the fits of the "pure" compound, but there is no magnetic ordering or spin fluctuations observed in the heat capacity data. The reduced specific jump $\Delta C/\Delta C_0$ at $T_C$ versus the reduced transition temperature $T_C/T_C^0$ follows neither the BCS prediction nor the Abrikosov and Gor'kov theory. We conclude that the compounds Lu$_2$(Fe$_{1-x}$Co$_x$)$_3$Si$_5$ are not BCS superconductors and spin fluctuations are not the reason for the depression of $T_C$.

The measurement of the dc electrical resistivity of the compound Lu$_2$Fe$_3$Si$_5$ and the 4 at.% and 8 at.% Co-containing samples show no minimum point in the resistivity data. The temperature dependence of the resistivity of the compound Lu$_2$Fe$_3$Si$_5$ is quadratic for $T<50K$ and proportional to $\ln T$ at high temperatures. For the Co-containing samples, the residual resistivity $\rho_{res}$ increases as expected while the temperature dependence deviates from a $T^2$ law at low temperatures and tends to increase linearly with $T$ at high temperatures. We conclude that a combination of complex scattering mechanisms are responsible for the unusual temperature dependence of $\rho(T)$. 
In summary, when transition metals such as Cr, Co and Ni are substituted for Fe in the compound Lu$_2$Fe$_3$Si$_5$, they lose their magnetic moment just as Fe did and thus behave as non-magnetic impurities. Co, a nominally magnetic transition metal, behaves differently from all other 3d transition metals but similarly to Ru in the compounds Lu$_2$(Fe$_{1-x}$T$_x$)$_3$Si$_5$. Mn and Cu substitutions form localized magnetic moments either at the impurity sites or on the Fe sites.

We conclude that the nature of the covalent bond between the Fe atom and its nearest neighbor Si atoms probably are related directly to the non-magnetic behavior of the iron atoms in Lu$_2$Fe$_3$Si$_5$-type superconductors. More experimental work are necessary for a complete understanding of the magnetic and electric properties of these compounds. Band structure calculations would be of great assistance in explaining the non-magnetic behavior of these transition metals in the compounds Lu$_2$(Fe$_{1-x}$T$_x$)$_3$Si$_5$. 
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VII. APPENDIX: SOURCES AND PURITIES OF STARTING MATERIALS

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<tr>
<th>Element</th>
<th>Source</th>
<th>Purity</th>
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<td>Lu</td>
<td>Ames Laboratory</td>
<td>batch 51585, rod</td>
</tr>
<tr>
<td></td>
<td></td>
<td>major impurities (atomic): Fe 45ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al 5ppm</td>
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<tr>
<td></td>
<td></td>
<td>W 5.6ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>all other impurities are less than 2ppm</td>
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<tr>
<td>Si</td>
<td>Research Organic/Inorganic</td>
<td>m7N5 pieces</td>
</tr>
<tr>
<td></td>
<td>Chemical Corp.</td>
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</tr>
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<td>Cr</td>
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<td>m4N8 crystallites</td>
</tr>
<tr>
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<tr>
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