Superconductivity in the lanthanum-yttrium-manganese alloy system

by

Roger Joseph Stierman

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
MASTER OF SCIENCE

Major: Metallurgy

Iowa State University
Ames, Iowa

1979

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ABSTRACT

An empirical approach involving lattice instabilities was investigated in the search for new superconducting materials. Pseudo-lanthanide compounds using La and Y were prepared for the system $La_{1-x}Y_xMn_2$ by arc melting and subsequent heat treatment. Low temperature magnetic susceptibility and low temperature heat capacity measurements were made. The unit cell lattice parameters were determined from x-ray powder patterns taken on most samples and metallographic examination was carried out on selected samples. Alloys with low La concentrations ($x \geq 0.6$) showed RMn_2 in the cubic C15 Laves phase as the major component with second phase material present. The magnetic susceptibility and x-ray data indicated a superconducting phase which seemed to be the RMn_2 phase, but heat capacity measurements showed the second phase material was the superconductor, while the RMn_2 was not. Failure to form compounds with higher La content was experienced and may be due to the lattice instability expected at $x = 0.56$. This indicates that perhaps more stingent conditions are required to form pseudo-lanthanide compunds than were previously considered. More systems should be investigated to see if this is true, and to determine the possibilities of this approach.

INTRODUCTION

In the search for new superconducting materials, many empirical approaches are tried. Matthias[1] and others have used guidelines such as preparing materials with certain valence electron to atom (e/a) ratios, selected crystal structures,[2] soft phonon modes,[3] or high density of states at the Fermi surface.[4] Many superconducting materials show polymorphism (e.g. $LaOs_2$ exhibits both the C14 and C15 Laves crystal structures, and is superconducting in both forms[5]) indicating a lattice instability. However, the existence of a lattice instability is not a sufficient condition for the occurrence of superconductivity, or vice versa.

Many lanthanide compounds exhibit polymorphism in the sequence between La and Lu. It was pointed out by Gschneidner[6] that the compounds near these crystal structure changes can be considered to have lattice instabilities, and may possibly be superconducting if no unpaired 4*f* electrons are present. Locations within the lanthanide series at which compounds begin to form or terminate are also points of lattice instability, and likewise possible superconductor candidates. However, most of these polymorphic changes occur several atomic numbers away from either end of the lanthanide series (La and Lu) and the presence of unpaired 4*f* electrons in the lanthanide metal prevents superconductivity.

It was suggested by Gschneidner that one might be able to make a lanthanide compound with no unpaired 4f electrons at one of these compositions removed from the endpoints of the series by forming the appropriate pseudo-lanthanide compound by using the proper proportions of La and Lu or La and Y. If the pseudo-lanthanide formed would correspond to the lanthanide compound at one of these points of lattice instability, there would be a high probability that it would also be superconducting. Even if one of the components of the pseudo-lanthanide does not form a compound with the others in the pure binary composition, the pseudo-compound would be expected to contain some of all the components used, since otherwise this would provide an easy method of separating some of the rare earth elements. A volume change in the unit cell of the pure La, Lu, or Y binary compound would be evidence that all components are present, as would a crystal structure change as the relative amounts of La and Lu or La and Y were varied.

La and Y were chosen as the rare earth elements to be used in the formation of the pseudo-lanthanide compounds. These were chosen because La itself is a fairly high T_c material (6 K at standard pressure, 10 K at high pressures) and most superconductors containing Y have higher T_c's than those containing Lu. The combination of La-Y would therefore be expected to have better superconducting properties in the pseudo-lanthanide compound as compared to La-Lu or Y-Lu pseudo-lanthanides. On the basis of size and alloying behavior of Y, Gschneidner suggested that Y in the pseudo-lanthanide would be similar to Dy, i.e. Y is pseudo-Dy.

THEORY

The system chosen for investigation was $La_{1-x}Y_xMn_2$. In the RMn_2 system (where R=rare earth) the compound does not exist for R = La, Ce, Eu, and Yb. From R = Pr to Sm the compounds have the hexagonal C14 Laves phase structure, from R = Sm to Ho the C15 cubic structure, and from R = Ho to Lu again the C14 structure.[7] Thus the compound series begins with $PrMn_2$, and is polymorphic at $SmMn_2$ and $HoMn_2$. YMn_2 forms the C15 structure, which is consistent with the representation of Y as pseudo-Dy. Using Y in place of Dy, there would be 8 elements between the 'endpoints' of La and Y when preparing a pseudo-lanthanide compound. To determine the composition parameter x for a particular pseudo-lanthanide of composition $La_{1-x}Y_xMn_2$, the following formula would be used:

x = (atomic number of lanthanide - atomic number of La)/9

If the elements La and Lu were used for pseudo-lanthanide formation, the number in the denominator of this equation would be 14 instead of 9, since there are 13 elements between La and Lu. Note, when using La and Y, only the atomic number of those lanthanides from La to Dy can be substituted in this manner. For example, a pseudo-lanthanide corresponding to Ce would have the following composition parameter x:

$x = (58 - 57)/9 = 0.111$

so pseudo-Ce would be $La_{.889}Y_{.111}$.

As mentioned earlier, the lattice instabilities in the RMn_2 system occur at R = Pr, Sm, and Ho. Since the atomic number of Ho is outside of the range of pseudo-lanthanides prepared with La and Y, the compositions at which the pseudo-lanthanides were expected to show superconductivity were $La_{.78}Y_{.22}Mn_2$ (pseudo-Pr) and $La_{.44}Y_{.56}Mn_2$ (pseudo-Sm). One would expect the superconducting transition temperature T_c to peak at these compositions, along with a crystal structure change between C14 and C15 Laves structures at pseudo-Sm.

In the binary systems of La-Mn, La-Y, and Y-Mn, La and Mn do not form any compounds and exhibit a eutectic at 17% at. Mn and 701 ^{o}C, and a monotectic at 88% at. Mn and 1081 ^{o}C.[8] La and Y form a α -Sm structure at 52% at. Y (pseudo-Sm is near 56% at. Y) and solid solutions between 0-35% at. Y and 60-100% at. Y.[9] Y and Mn form three compounds, YMn_2, Y_6Mn_{23}, and YMn_{12}. YMn_2 is paramagnetic, Y_6Mn_{23} is ferrimagnetis with a Curie temperature of 468 K[10], and YMn_{12} is antiferromagnetic with a Néel temperature of 120 K.[11]

EXPERIMENTAL

The La and Y used were prepared in this laboratory by calcium reduction of the fluoride followed by vacuum casting for La and vacuum distillation for Y. Several batches of La and Y were used, and the major impurities are listed in Tables I-III. The Mn used was supplied by Mr. Frederick Schmidt as sublimed, and showed major impurities of 35 ppm C and 41 ppm O.

Samples for each composition were weighed and arc melted under a gettered He or Ar atmosphere. Because Mn has the highest vapor pressure of all the components at the melting temperature, any weight loss encountered when the samples were arc melted was assumed to be due to Mn loss. As an example, a sample prepared with composition $La_{.33}Y_{.67}Mn_2$ started with 1.5627 g. La, 1.9833 g. Y, and 3.6948 g. Mn for a total weight of 7.2408 grams. The final weight of this button after arc melting was 7.2086 g. This corresponds to a loss of 0.0322 g. Mn- about 1% of the weight of Mn used, or 0.5% of the total weight of the sample.

A weight loss of this order (between 0.5 -2%) was typical for all samples. Because Mn is lighter than Y or La, though, this weight loss would be comparable to 5% at. loss of Mn. In the attempts to minimize Mn losses, two methods were tried to achieve the best arc melting results. The first method was to melt in one operation the proper amounts of La, Y, and

TABLE I

Mass spectrometric, vacuum fusion, and chemical analysis of La-42176

Element	Impurity level, ppm atomic
P	511
H	275
O	252
C	93
Ni	22
N	20
Cu	6.9
Fe	6.2
Si	6
Ce	5
Cr	4
Na	3
Cl	3
Y	2.6
Ta	2.4
W	2
Mo	1

TABLE II

Mass spectrometric, vacuum fusion, and chemical analysis of La-102877

Element	Impurity level, ppm atomic
N	545
H	412
O	304
P	180
C	92
Cl	10
Fe	4
Ta	2
Cu	1.8
Sc	1
Ce	1

all others less than 1 ppma

TABLE III

Vacuum fusion analysis of Y-101672

Element	Impurity level, ppm atomic
H	530
O	860
N	207

Vacuum fusion and chemical analysis of Yttrium, JC-4-85

Element	Impurity level, ppm atomic
O	900
H	410
F	350
C	300
Fe	16

Mn with the rare earth metals on top of the Mn. The arc would then be drawn from the rare earth metals, which would melt and flow around the Mn, thus reducing the amount of vaporization of Mn. The second method was to melt the La and Y in the proper proportions into a master alloy (e.g. such as pseudo-Sm). Then portions of the master alloy were melted with the correct weight of Mn, again striking the arc first on the rare earth alloy which would flow around the Mn. With either method, the weight loss and homogeniety of the as-cast buttons was essentially the same, so the first method was used most of the time.

Each melt contained phases other than the desired RMn_2, which is similar to the results obtained by Marei et al. in their study of YMn_2[12]. A R_6Mn_{23} compound formed directly from the melt, as well as RMn_2 and free rare earth. The as-cast buttons exhibited some ductility, such as flattening when pounded in the steel mortar, making it difficult to crush samples on the preparation of X-ray powder pattern samples. To eliminate the unwanted phases, the buttons were wrapped in Ta foil, sealed in Ta crucibles under a partial He atmosphere, and annealed to try and produce single phase RMn_2. Different heat treatments were tried using temperatures between 750-1000 °C and times between 24-300 hours. For compositions between $0.6 \leq x \leq 1$ the best results were obtained at 900-950 °C, holding for 100-200 hours. Samples with lower La content

could be heat treated at the higher temperature with correspondingly shorter times, but samples with higher La contents ($x \leq 0.6$) would stick to the Ta foil, or run out of the foil and be lost, unless the temperature was held below 900 °C.

X-ray diffraction powder patterns of the heat-treated samples, and initially of the as-cast samples, were taken using Debye-Scherer cameras. For compositions with $0.6 \leq x \leq 1$ the heat-treated buttons could be crushed fairly easily, with little or no evidence of residual strain noted in the powder pattern. These samples were essentially single phase RMn_2 as observed in the powder patterns, and a typical pattern from this composition range is indexed in Table IV. Samples with composition $x \leq 0.6$ exhibited some ductility even after heat treatment, and would flatten noticeably before cracking when crushed in the steel mortar. Powder patterns from these samples showed many lines in addition to the RMn_2 lines. Furthermore, since the samples were sufficiently strained during crushing, the lines in the back-reflection region of the patterns were not well resolved. Most of the extra lines were indexed as R_6Mn_{23} phase, but some of the lines could not be indexed as belonging to either RMn_2 or R_6Mn_{23} patterns. These lines were probably due to unreacted Mn or rare earth.

Portions of the heat-treated samples, and some of the as-cast samples were sealed in quartz or Pyrex glass capsules

TABLE IV

Some crystallographic data for $La_{.33}Y_{.67}Mn_2$ powder pattern using Cu $K\alpha$ radiation, a_o = 7.702 Å

θ	$\sin^2\theta$	hkl indices
16.366	0.07939	220
19.299	0.10922	311
20.176	0.11896	222
29.301	0.23951	422
31.256	0.26922	511, 333
34.365	0.31861	440
39.203	0.39951	620
40.958	0.42968	533
41.534	0.43966	622
48.503	0.56099	642
50.258	0.59126	731, 553
53.166	0.63979	800
	the following are $K\alpha_1$, $K\alpha_2$ pairs	
	0.71965	
58.029	0.72278	822.660
58.230		
59.960		
59.960	0.74939	
60.286	0.75430	751.555
72.369	0.90826	
72.995	0.91447	931
78.360	0.95929	
79.087	0.96416	844

under He atmosphere and measured for their low-temperature magnetic susceptibility. These measurements were done by Dr. Finnemore's group using a modified A.C. Hartshorn bridge operated at a frequency of 100 Hertz. From these measurements, the superconducting transition temperature, T_c, was defined as the point where the output of the bridge was halfway between the maximum and minimum values for each particular transition. The tops of the glass capsules were broken before measurements were made to ensure there was good thermal contact between the samples and the helium cooling bath.

Low temperature heat capacity measurements were made in the 1-10 K temperature range using an adiabatic heat-pulse type calorimeter. The samples used were heat-treated buttons which were ground flat on their broad dimension, with button weights of about 3.5 - 4 g. The results were plotted on a scale of heat capacity over temperature versus temperature squared (C/T vs. T^2), because this plot is most sensitive to heat capacity anomalies, such as those due to superconductivity or magnetic ordering. At the same time, the values of the lattice specific heat (β), which gives the Debye temperature (θ_D), and the elctronic specific heat (γ) can be extracted from such a plot. The units for the heat capacity are given in millijoules per gram-atom per degree Kelvin (mJ/ gm-at.K).

Metallography was done by Mr. Harlan Baker of the Metal-

lography Service Group. Mechanical polishing of the cut or ground surfaces followed by a perchloric acid in absolute methanol electropolish was sufficient to disply the phases present.

RESULTS

Table V lists the compositions of the samples made, the superconducting transition temperatures, and the change in the relative susceptibility when each samples goes superconducting. Samples with compositions $x \leq 0.9$ exhibited superconductivity above 1 K, increasing from 1.5 K at $x = 0.9$ to 3.2 K at $x = 0.6$ for the lower temperature superconducting transition. A second transition is observed at $x = 0.78$ and has a constant temperature of 4.5 K for the composition range $0.22 \leq x \leq 0.78$. The lower part of Fig. 1 shows a plot of superconducting transition temperature T_c vs. composition parameter x. It is noted that the lower temperature transition is constant at 3.2 K for $x \lesssim 0.6$.

The upper part of Fig. 1 displays a plot of lattice parameter a_o vs. composition x for the cubic C15 phase formed. The dashed line represents the expected theoretical lattice parameter expansion based on the relative sizes of La and Y atoms, while the solid line is a closest-fit straight line through the experimental data points (open circles). The observed line lies below the theoretical line, but the expansion of the lattice parameter as the La composition fraction increases shows that some La is present in the RMn_2 phase. The x-ray data points were taken only for samples with compositions in the range $x \gtrsim 0.6$ because samples with $x \leq 0.6$ would not produce x-ray patterns of sufficient quality to

TABLE V

Relative susceptibility and temperature at % superconducting for heat-treated samples

Composition	90%SC	50%SC	10%SC	$\Delta\chi$, emu/cc
$La_{.8}Y_{.2}Mn_2$	4.67	5.39	5.77	$1.4x10^{-2}$
$La_{.78}Y_{.22}Mn_2$	2.86 4.23	3.18 4.46	3.52 4.73	$3.5x10^{-3}$ $5.3x10^{-3}$
$La_{.75}Y_{.25}Mn_2$	4.11	4.46	4.82	$1.3x10^{-2}$
$La_{.6}Y_{.4}Mn_2$	4.15	4.34	4.65	$1.2x10^{-2}$
$La_{.5}Y_{.5}Mn_2$	2.58	3.07	3.28	$1.0x10^{-2}$
$La_{.44}Y_{.56}Mn_2$	2.64 4.03	2.83 4.64	2.97 5.21	$0.9x10^{-3}$ $0.6x10^{-3}$
$La_{.4}Y_{.6}Mn_2$	2.69 3.98	3.18 4.54	3.42 4.84	$1.2x10^{-2}$ $3.8x10^{-3}$
$La_{.33}Y_{.67}Mn_2$	2.75	3.09	3.24	$1.9x10^{-2}$
$La_{.3}Y_{.7}Mn_2$	2.23 4.34	2.84 4.64	3.26 4.95	$5.0x10^{-3}$ $3.5x10^{-3}$
$La_{.22}Y_{.78}Mn_2$	2.36	2.53	2.64	$7.5x10^{-3}$
$La_{.11}Y_{.89}Mn_2$	was not superconducting above 1 K			
$La_{.1}Y_{.9}Mn_2$	1.37	1.47	2.23	$4.5x10^{-3}$
YMn_2	was not superconducting above 1 K			

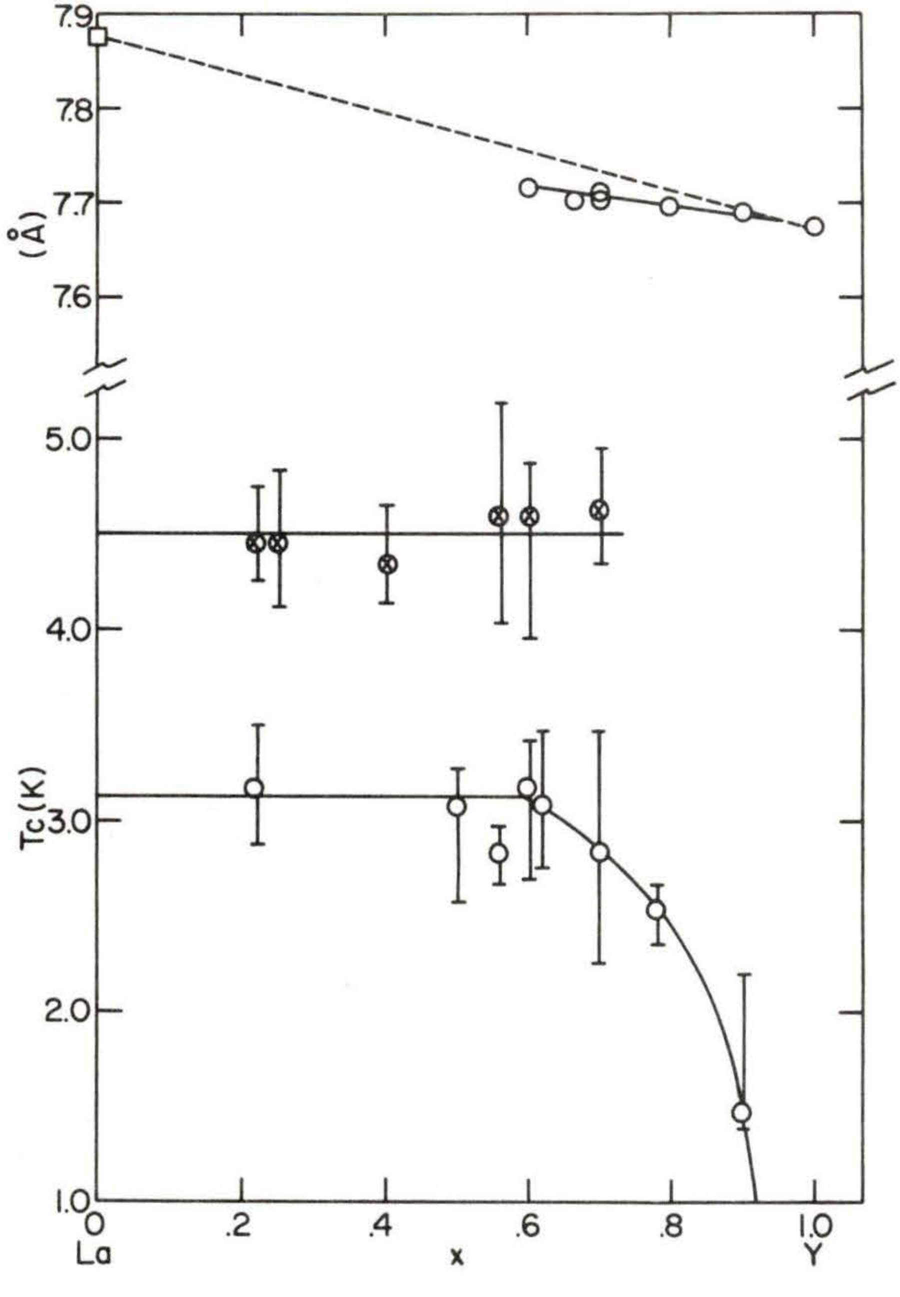


Fig. 1. Variation of T_c and a_o with composition.

interpret. All of the lattice parameters used for data points in Fig. 1 were refined from the powder patterns using the Nelson-Riley extrapolation function. Table VI lists the lattice parameters obtained for each composition.

Metallographic examination shows the presence of some second phase in all samples. Fig. 2 is a set of 100X photomicrographs taken of some of the heat-treated samples. The as-cast samples always had a large amount of second phase, which was also evident from the x-ray patterns. The white areas visible in the photomicrograph is probably RMn_2, while the gray areas in between the white grains (e.g. in the $La_{.1}Y_{.9}Mn_2$ micrograph, Fig. 2b) is RMn_2-rare earth or RMn_2-R_6Mn_{23} eutectic. In samples with high La content (e.g. $La_{.6}Y_{.4}Mn_2$, see Fig. 2d) the dark areas between the white grains are voids, and the gray rimming around the white grains is probably R_6Mn_{23}. These interpretations were made because the presence of both RMn_2 and R_6Mn_{23} is known to occur in the samples with composition $x \leq 0.6$ from the x-ray data. It is significant to note that x-ray patterns of heat-treated samples did not indicate the existence of second phase for compositions $x \geq 0.6$, but these photomicrographs demonstrate the presence of second phase.

Because the magnetic susceptibility measurement used to determine T_c is sensitive to small amounts of superconducting phases present, a measurement of the bulk superconductivity

TABLE VI

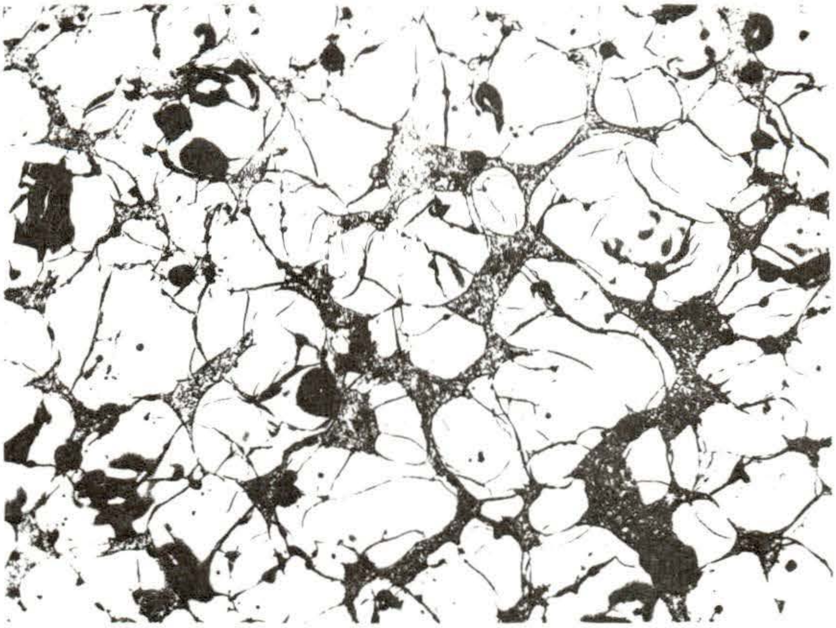
Lattice parameters of heat-treated samples

Composition	a_o, Å ± 0.001 Å
YMn_2	7.678
$La_{.1}Y_{.9}Mn_2$	7.693
$La_{.2}Y_{.8}Mn_2$	7.697
$La_{.3}Y_{.7}Mn_2$, #1	7.698
$La_{.3}Y_{.7}Mn_2$, #2	7.702
$La_{.33}Y_{.67}Mn_2$	7.702
$La_{.4}Y_{.6}Mn_2$	7.702

Fig. 2. 100 X photomicrographs of selected samples

a. YMn_2, heat treated 1000 °C, 100 hours

b. $La_{.1}Y_{.9}Mn_2$, heat treated 800 °C, 200 hours



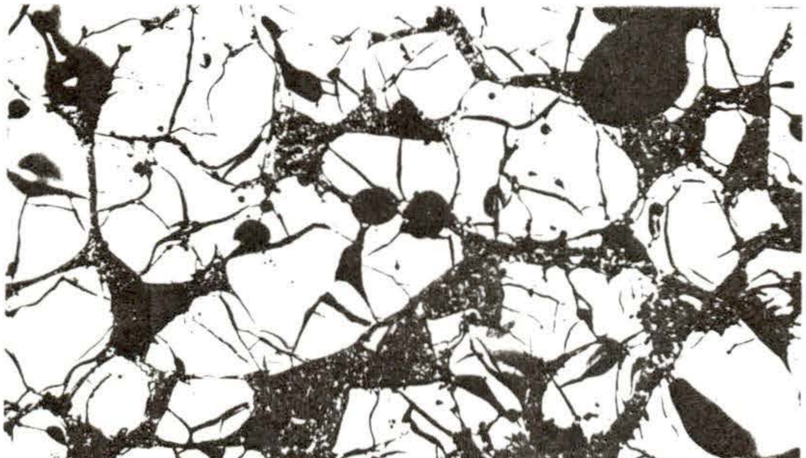
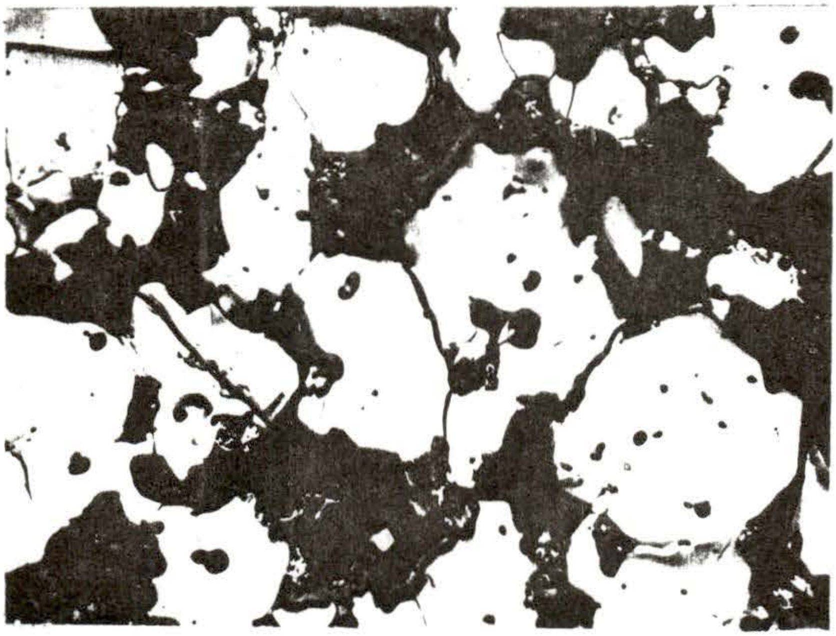


Fig. 2 (continued)

c. $La_{.22}Y_{.78}Mn_2$, heat treated 750 °C, 200 hours

d. $La_{.6}Y_{.4}Mn_2$, heat treated 850 °C, 150 hours



was needed, to see if the superconductivity observed was due to an impurity phase, or the major component of the alloy (RMn_2). The low temperature heat capacity measurement of a superconductor shows a peak in the heat capacity curve at the superconducting transition temperature, where the material changes between the superconducting and nonsuperconducting states[13]. Four samples, two of composition $La_{.22}Y_{.78}Mn_2$ and one each of $La_{.44}Y_{.56}Mn_2$ and $La_{.78}Y_{.22}Mn_2$, were measured for low temperature heat capacity in the 1-10 K region, and the resultant curves are shown in Fig. 3. In the case for $x = 0.22$ peaks are observed at 4.5 and 5.7 K (20.25 and 32.5 respectively in terms of T^2), but not at 3.2 K (10.24 in T^2). This was the first sample in which heat capacity was measured, and because it contained more 'impurity' phase than the desired RMn_2, it was not a good choice of samples. The measurement of the first sample with composition $x = 0.78$ shows a small peak at 2.5 K (6.25 in T^2), while the second sample of this composition had no anomalous heat capacity behavior, i.e. no superconductivity was observed in the heat capacity data above 1 K. The last sample measured, with $x = 0.56$, also showed no anomalous heat capacity above 1 K.

Values of the heat capacity constants (the lattice term β and the electronic term γ) were extracted from the C/T vs. T^2 plots, and are listed in Table VII. For those samples which showed superconductivity, the values of the jump in

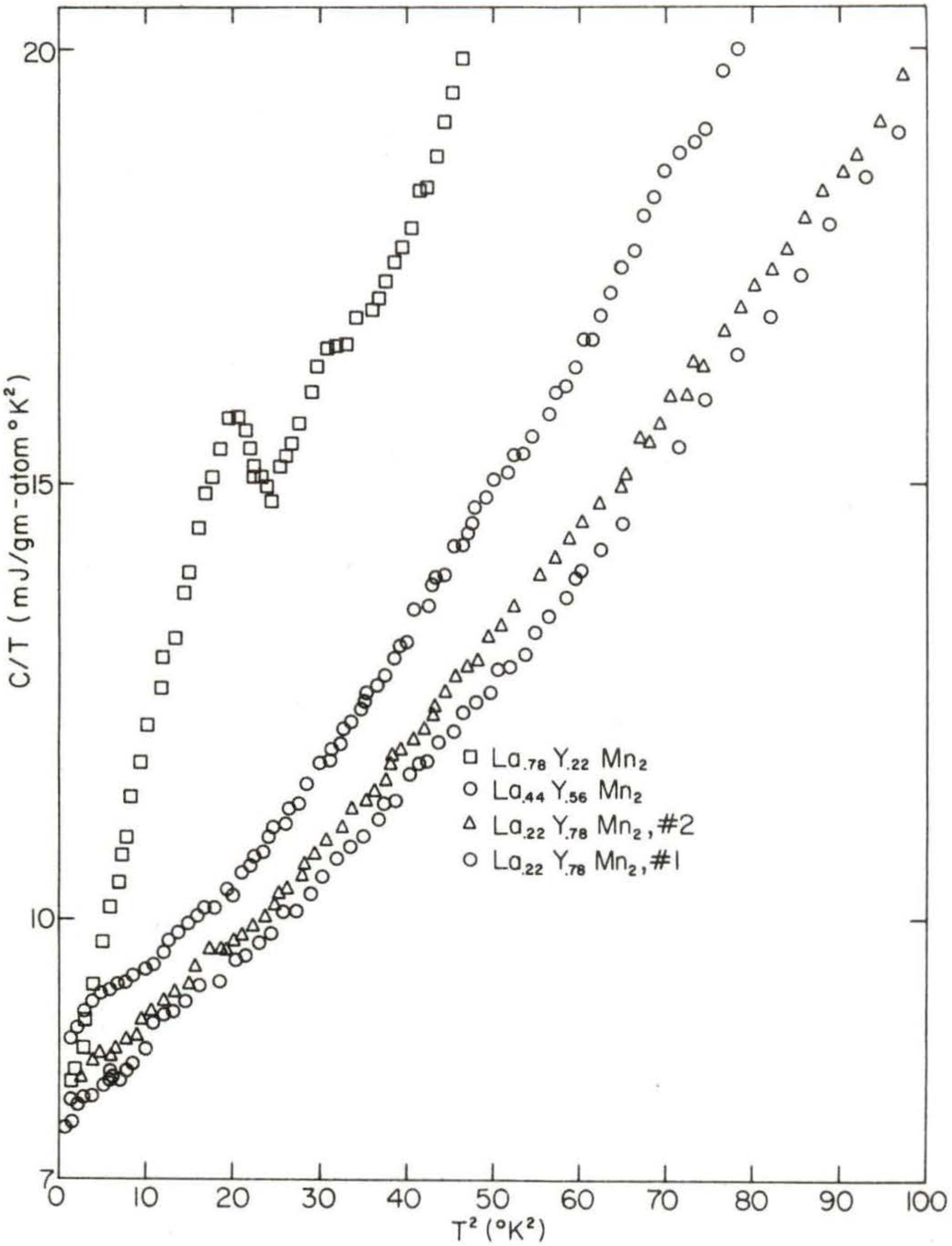


Fig. 3. Heat capacity data for compositions measured.

TABLE VII

Values of the lattice and electronic heat capacity contributions from the heat capacity data

Composition	β	γ	θ_D	$\Delta C_p/\gamma T_c$
$La_{.78}Y_{.22}Mn_2$	0.4[a]	7.33[a]	169	0.48
$La_{.44}Y_{.56}Mn_2$	0.094	8.55	274	0
$La_{.22}Y_{.78}Mn_2$, #2	0.0921	7.90	276	0
$La_{.22}Y_{.78}Mn_2$, #1	0.09[a]	7.7[a]	278	0.06

[a] These results are not very reliable because they were not lease-squares fitted due to the superconducting transition.

heat capacity at the superconducting transition are also listed. According to BCS (Bardeen-Cooper-Schreifer) theory, the change in heat capacity at T_c (versus the normal state) should be given by

$$\Delta C_V = 1.52\,\gamma T_c, \text{ or } \Delta C_V/\gamma T_c = 1.52,$$

if the whole sample is superconducting. Comparing the values of $\Delta C_V/\gamma T_c$ in Table VII, it is observed that $\Delta C_V/\gamma T_c$ is much smaller than 1.52, and is more on the order of .06-.48 (5-30% of the expected value of 1.52). This suggests that only about 5-30% of the samples are superconducting at these temperatures if the superconducting phase behaves as a BCS type superconductor. Even if the superconducting phase is not a BCS type superconductor, the low values of $\Delta C_V/\gamma T_c$, especially for the alloy composition $La_{.22}Y_{.78}Mn_2 = 1$, indicate only a portion of the samples are superconducting.

DISCUSSION

From the T_c and x-ray data alone it appeared that the expected lattice instability of $La_{1-x}Y_xMn_2$ at x = 0.56 had occurred, and that as a result of the instability, this phase was a superconductor. The concurrent increase in lattice parameter a_o and superconducting transition temperature T_c as x decreased was considered to be sufficient evidence to verify this conclusion. In view of the metallography and heat capacity data, however, the compound formed is not superconducting, at least above 1 K. Metallography and x-ray data show the major phase formed between $0.6 \leq x \leq 1$ is RMn_2, since this phase can be seen in the series of micrographs of Fig. 2 and the x-ray Debye-Scherer patterns. The amount of second phase material observed in the photomicrographs (approximately 10%) is about the same as the amount of superconducting material as determined by the heat capacity measurements. Thus it is the second phase, and not the RMn_2 compound, which is superconducting between 1.5-3.2 K. La-Y alloys have different superconducting transition temperatures, depending on the composition, and the second phase is probably these alloys. For example, a T_c of 1.5 K corresponds to a composition of $La_{.60}Y_{.40}$, while $La_{.85}Y_{.15}$ has a T_c of 3.2 K[14]. The presence of this alloy would also be evident in the heat capacity measurements. $La_{.75}Y_{.25}$ has T_c of 2.0 K and a jump in heat capacity at T_c of about 16 mJ/g-at.K, corresponding to

$\Delta C_p / \gamma T_c$ of 1.3.[15] This shows that a small amount of the superconducting phase is detectable in the heat capacity data, but in this case (as opposed to magnetic susceptibility measurements) a rough measure of the amount of superconducting material can be determined.

The lack of superconductivity in the RMn_2 compound may be due to the low La concentration ($x \geq 0.6$) in the pseudo-compound. Considering, (1) no compounds having more than 50% at. Mn are known to be superconducting,[16] and (2) the superconductivity in the Laves phases is carried by the B (Mn) element,[17] it would be thought no superconductivity would be found regardless of the nature of the A (La, Y) element. It is possible, though, with higher La concentrations ($0.4 \geq x$) superconductivity might be observed, i.e. if the pseudo-Pr compound had been formed ($La_{.78}Y_{.22}Mn_2$). This was not observed because no RMn_2 compounds could be formed for the high La compositions ($0.4 \geq x$).

Besides the lattice instability at $x = 0.56$, the difficulty in forming pseudo-lanthanides with high La content may be due to the failure of La to form a compound in this series. This may mean that a lattice instability at the beginning or termination of compound formation is too large an instability to allow pseudo-lanthanide formation nearby. If both of the endpoints of the pseudo-lanthanide series had formed compounds, then a continuous series of compounds as the compositions were varied should be observed. Thus, a better test of the pseudo-lanthanide lattice instability concept would be the study of a system in which both La and Y, La and Lu, or Y and Lu formed compounds, with a crystal structure change in between, e.g. YMn_2-$LuMn_2$. As mentioned previously, a pseudo-lanthanide involving La and Y would be expected to have better superconducting properties than the others, so a pseudo-lanthanide using La and Y with compound formation by both rare earth elements should be investigated.

CONCLUSIONS

The expected result of superconductivity associated with a lattice instability of a pseudo-lanthanide compound was not realized because the pseudo-lanthanide compound desired was not formed. This was the first system so investigated, though, so the concept of superconductivity at a pseudo-lanthanide lattice instability is not yet ruled out. What this study appears to find is the more rigid requirement that both elements at the endpoints of the pseudo-lanthanide series form compounds. This additional requirement restricts the available systems for study, but there are systems which satisfy this requirement and may prove interesting (e.g. ROs_2, which has polymorphisms at R = La, Ce, and Pr, while only $LaOs_2$ is superconducting). Systems using La and Lu or Y and Ly should also be tried, since the assumption that La-Y alloys have better superconducting properties may have exceptions. More work must be done to develop this empirical approach to its fullest capabilities.

REFERENCES

1. Matthias, B.T., Phys. Rev. 1955, 97(1), 74.

2. Hartsough, L.D., *J. Phys. Chem. Solids* 1975, 35, 1691.

3. Hulm, J.K.; Walker, M.S.; Pessal, N., *Physica* 1971, 55,60.

4. Dynes, R.C.; Varma, C.M., *J. Phys. F.:Metal Phys.* 1976, 6(7), L215.

5. Lawson, A.C.; Cannon, J.C.; Robertson, D.L.; Hall, H.T., *J. Less-Common Metals,* 1973, 32, 173.

6. Gschneidner, K.A., Jr., "From Infinity to Zero and Back Again to Infinity (From Mixed Rare Earths to Ultrapure metals to Pseudo-Lanthanides)", 14th Rare Earth Research Conference, June 1979, Fargo, N.D., in press.

7. Iandelli, A.; Palenzona, A., in "Handbook on the Physics and Chemistry of Rare Earths", K.A. Gschneidner, Jr. and L. Eyring Eds., North-Holland Publishing Co.: Amsterdam, 1979; Vol. II, Chapter. 13.

8. Gschneidner, K.A., Jr., "Rare Earth Alloys", D. Van Nostrand Co.: Princeton, 1960; Chapter II-3.

9. Spedding, F.H.; Valletta, R.M.; Daane, A.H., *Trans. Quarterly* 1962, 55(3), 483.

10. James, W.J.; Hardman, K.; Yelon, W.; Kebe, B., *Journal de Physique* 1979, 40(5), C5-206.

11. Deportes, J.; Givord, D.; Lemaire, R.; Nagai, H., "Magnetic Interactions in the RMn_{12} Compounds", Proceedings of the International Conference on Magnetism, 1976, pp 69-70.

12. Marei, S.A.; Craig, R.S.; Wallace, W.E.; Tsuchida, T. *J. Less-Common Metals* 1967, 13, 391.

13. Kittel, C., in "Introduction to Solid State Physics", 2nd ed., John Wiley and Sons: New York, Chapter 16.

14. Anderson, G.S.; Legvold, S.; Spedding, F.H., *Phys. Rev.* 1958, 109, 243.

15. Sotoh, T.; Ohtsuka, T., J. Phys. Soc. Japan 1967, 23, 9.

16. Roberts, B.W., J. Phys. Chem. Ref. Data 1976, 5(3), 581.

17. Wilhelm, M.; Hillenbrand, B., J. Phys. Chem. Solids 1970, 31, 559.

ACKNOWLEDGEMENTS

I would like to thank my major professor, Dr. Karl A. Gschneidner, Jr., for introducing me to the topic of this thesis, and for his direction and clarifications in the interpretation of the information obtained, and to Mr. O. Dale McMasters for his help and comments in obtaining the materials, sample preparation, and x-ray analysis. I would also thank Dr. Douglass K. Finnemore and Mr. Jerry Ostenson for the magnetic susceptibility measurements and helpful comments about them, Mr. Paul Palmer for the reduction, Mr. Robert Conzemius for the spectrometric analysis of the rare earth metals used, and Mr. Harlan Baker for the metallography of the samples. This work was supported by the U.S. Department of Energy, Office of Basic Energy Science, Division of Material Sciences.