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SUPERCONDUCTIVITY OF
LANTHANUM AND SOME LANTHANUM ALLOYS

by

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INTRODUCTION

The phenomenon of superconductivity remains as one of the major unsolved problems of modern physics. There have been several recent notable attempts to explain superconductivity, for instance, the theories of Bardeen (1950) and Fröhlich (1950). However, none of these theories are capable of satisfactorily predicting the temperature at which a substance will become superconducting, or indeed whether it ever will. It is known that certain properties of matter, such as the molecular volume, the molecular mass, the number of conduction electrons, the internal magnetic field, and the crystal structure play a very important, although not well understood, role in superconductivity. Quantitative information concerning the effects of these factors should enable one to better understand this low temperature phenomenon.

In the work reported here the importance of the molecular volume and the molecular mass in superconductivity was examined by alloying lanthanum with yttrium, lutetium, and ytterbium. Lanthanum and lutetium have the same three conduction electrons; their unlikeness in electron configuration occurring in the $4f$ band (being completely empty for lanthanum and completely filled for lutetium) which presumably does not participate directly in the conduction process. By this alloying the molecular

volume and the molecular mass may be varied while the number of conduction electrons per atom remains unchanged. A similar study is possible by alloying lanthanum with yttrium which also has three conduction electrons; however, these are in the 4d and 5s bands, whereas those of lanthanum and lutetium are in the 5d and 6s bands.

One alloy of lanthanum and ytterbium was studied. Ytterbium might be expected to have thirteen 4f electrons since it is next to the last of the lanthanide series; however, the divalent state with a completed 4f band has lower energy. Hence for this study one would be varying the electron density as well as the mass and volume. A structure analysis of the alloys studied was made, since crystal structure is known to be important in superconductivity.

Lanthanum is the only known superconductor of the four elements used for this work. At least two crystal structures of lanthanum are superconducting with different transition temperatures; hence a study of these was made. Critical field measurements were performed for cubic lanthanum.

REVIEW OF LITERATURE

Fundamental Theories

There exists no universally accepted fundamental theory of superconductivity. Various theories have been proposed, but none are entirely capable of accounting for the actual properties of superconductors. It has been believed that the reason for this difficulty lies in the fact that electron-electron interactions are usually ignored. The conventional treatment is to consider one electron in a periodic potential field in order to simplify the problem. Different types of interactions which may give rise to the onset of superconductivity have been considered. We may mention briefly some of these theories.

The first theory considering electron interactions was proposed in 1947 by Heisenberg (1947) who considered the ordinary Coulomb interaction between electrons. According to this theory this interaction produces, at low temperatures, a distortion of the ordinary Fermi distribution of electrons in momentum space such that a permanent current would exist in a domain. With no field applied the entire specimen should have zero net current since supposedly there are many domains of various orientations. A net current would exist when the domains are at least partially aligned as the result of an applied field. However, there are several aspects of this theory which

indicate that it is at least not entirely correct. For one thing an unpublished theorem of Bloch, discussed by others such as Bohm (1949), says that the lowest energy state of a quantum-mechanical system in the absence of a magnetic field can carry no current. Heisenberg argued that this theorem applies for macroscopic regions and need not apply for microscopic regions such as his domains. However, even if we ignore this question there are other difficulties in this theory. The permanent current density in a domain goes to zero at absolute zero. This would mean that the penetration depth for thin films should increase at high fields and low temperatures, which has not been observed. The theory also predicts superconductivity in all metals.

The next year Born and Cheng (1948) proposed a theory which included the interaction of electrons with the ionic lattice. As a basis for this theory they used the Brillouin zone model rather than the free electron gas model as employed by Heisenberg. They found an empirical rule which indicates a correlation between superconductivity and the lattice structure. This is that superconductors are those substances for which the Fermi sphere lies close to a corner of a Brillouin zone. The interaction of the electrons with the ionic lattice is appreciable only near the boundaries of a Brillouin zone, and especially near the corners. This theory can suggest why some materials

are superconducting and others not. It also suggests how the structure may influence superconductivity. However, it is difficult to see how the actual properties of a superconductor can be obtained from this description.

More recently, Fröhlich (1950) proposed a theory involving a somewhat different type of electron interaction. Associated with the scattering of electrons by phonons is the absorption or emission of vibrational quanta which gives rise to a self-energy. This interaction leads to an effective interaction of electrons in momentum space which is much smaller than the Coulomb interaction. Fröhlich argues that the Coulomb interaction is very important in cohesion but plays no role in this phenomenon. If Fröhlich's effective interaction is sufficiently strong, there will be a distribution of electrons in momentum space which is different from the normal Fermi distribution. This new distribution is supposed to be the superconducting one, according to Fröhlich who did a zero degree Kelvin calculation. The difference in energy between this state and the normal one is inversely proportional to M , the isotopic mass. This energy is also equal to $H_c^2/8\pi$ per unit volume, which one can obtain by thermodynamic considerations of a perfect diamagnetic substance. Thus H_c should vary as $M^{-1/2}$ and presumably also T_c . Later experiments, such as those of Maxwell (1950) and Reynolds, Serin, Wright, and Nesbitt (1950), indicated that T_c is at least approximately

proportional to $M^{-1/2}$ which is evidence tending to show that the interaction investigated here is the important one. The condition for superconductivity according to this theory is that $\rho n \nu^{5/3}$ ($1/n$ = atomic volume, ν = number of free electrons per atom, ρ = electrical resistivity at 0° C) exceed a certain value. All monovalent metals except lithium should be nonsuperconductors, which they actually are, according to this condition. However there are many exceptions to this condition. Also it is not too clear how the actual properties of a superconductor can be obtained from this state described by Fröhlich.

Another theory was proposed about the same time as Fröhlich's by Bardeen (1950) which is also based on the electron-phonon interaction. He developed his theory in a somewhat different way from Fröhlich. He considered a very small electron effective mass to describe the superconducting state. His condition was that $\nu \rho n > 10^6$ (ν = chemical valence taken as being equal to the group of the element in the periodic table, ρ = electrical resistivity in e.s.u., n = number of atoms per unit volume). This criterion, like that of Fröhlich's, is not especially good.

These latter two theories are the ones in most favor at the present time, since the isotope effect suggests that the electron-phonon interaction is the important one. Neither has been developed for finite temperatures. Hence

it can be seen that the fundamental theories of superconductivity are not capable of explaining superconductivity satisfactorily.

Criteria for Superconductivity

We have seen that the fundamental theories of superconductivity are not able to explain this phenomenon satisfactorily. In such cases one often examines certain empirical relations in the hope of obtaining a key to factors which are important in the phenomenon. One would like to have a criterion for superconductivity which would indicate whether or not a particular substance ought to be a superconductor. We have noted the inadequacies of the criteria of Fröhlich (1950) and Bardeen (1950).

A much earlier correlation was observed by Kikoin and Lasarew (1932) who found that both the Hall coefficient at room temperature and its product with the electronic conductivity at room temperature are in general small for superconductors. This is a somewhat better criterion than those of Fröhlich and Bardeen.

Groetzinger, Kahn, and Schwed (1954) used a somewhat different criterion. They used the freedom number, f , defined by the equation $f = n_f eR/c$ where n_f is the number of free electrons per unit volume (obtained from measurements of the refractive index and the optical absorption

coefficient), e is the electron charge, c is the velocity of light, and R is the room temperature Hall coefficient. It was found that the elements with freedom numbers between +0.15 and -0.16 are superconductors. This correlation was very good for the elements examined. A somewhat similar quantity $\gamma = (n/n_f)f$, where n is the number of atoms per unit volume, was used for more correlations because it could be calculated for many more elements. The value of γ for superconductors lies between +0.5 and -3.4. The non-superconductors having a γ in this range are nearly always transition elements which are ruled out for other reasons. This seems to be a better criterion than the others. These authors claim that a small value of f occurs if the Fermi surface intersects a Brillouin zone boundary such that the hole and electron contributions tend to cancel. This intersection implies a strong interaction between the conduction electrons and the ionic lattice, as was earlier discussed by Born and Cheng (1948).

Other criteria for superconductivity have been discussed recently by Matthias (1953 and 1955). In studying the transition temperatures of various elements and compounds he has found a dependence of the transition temperature on mass, volume, and the number of valence electrons per atom. He has found that the transition temperature varies inversely as the mass. This is quite different from the isotope effect where the transition temperature is

found to vary inversely as the square root of the isotopic mass. He also observed that the transition temperature should vary with the volume to some power between four and ten. The third correlation was that optimum conditions exist for superconductivity when the number of valence electrons per atom was either five or seven. The number of valence electrons per atom used is the number of electrons outside a closed shell according to its electron configuration. For instance tellurium would have six valence electrons per atom. There seems to be some justification for these criteria in the sense that they appear to have some validity when applied to many different substances. However these correlations are purely empirical and have no theoretical justification. They are valuable in the sense that they indicate the importance of certain factors on superconductivity and also suggest new experiments.

Lanthanum

There has been considerable disagreement concerning the superconductivity of lanthanum. In 1930 McLennan, Allen, and Wilhelm (1930) found no evidence of superconductivity above 1.9°K for lanthanum by measuring its electrical resistivity. Mendelsohn and Daunt (1937) first observed the superconducting transition by a magnetic method and found a transition temperature of 4.71°K . The analysis of their sample was given as 98 per cent

lanthanum, 1 per cent iron, and traces of carbon, silicon, aluminum, and magnesium. The magnetic field strengths at which the last trace of superconductivity disappeared were found to be very high (> 1000 oer. deg.⁻¹).

Shoenberg (1937), using an a.c. method, reported lanthanum to be superconducting at 4.2°K , but found that the critical field values were very indefinite.

Ziegler (1948) discovered superconductivity in two samples of lanthanum by studying the temperature dependence of their magnetic permeability. One sample, reported to contain 0.8 per cent iron, was found to have a transition temperature of $4.85 \pm 0.15^{\circ}\text{K}$. The second sample, reported to contain between 0.5 and 1 per cent aluminum, silicon and tungsten, was found to have a transition temperature of $4.45 \pm 0.10^{\circ}\text{K}$.

The specific heat of lanthanum was measured by Parkinson, Simon, and Spedding (1951). The impurities of their specimen were reported as follows: calcium, less than 0.05 per cent; beryllium, less than 0.01 per cent; and iron, less than 0.002 per cent. A room temperature x-ray study of the structure of the sample showed lines corresponding to both hexagonal close-packed and face-centered cubic structures. The transition temperature was observed to be

$$4.71^{\circ}\text{K} \text{ and } \left. \frac{dH_c}{dT} \right|_{H_c=0} = 280 \text{ oer./deg.}, \text{ using specific heat data.}$$

James, Legvold, and Spedding (1952) measured the electrical resistivity of two samples of lanthanum and found transition temperatures ranging from 5.5°K to 6.0°K depending on the heat treatment. The widths of the transitions varied from 0.3 degree to 0.9 degree.

Ziegler, Young, and Floyd (1953) made a study of the crystal structure and the superconductivity of lanthanum. They concluded that two structures of lanthanum are superconducting with different transition temperatures. They suggested that the face-centered cubic structure has a transition temperature of 5.4°K , whereas the hexagonal close-packed structure should have a transition temperature somewhat above 3.9°K .

EXPERIMENTAL PROCEDURE

Detection of Transition

Superconductivity was first observed by Onnes (1911) who was studying the electrical resistivity of mercury. Much later Meissner and Ochsenfeld (1933) discovered the perfect diamagnetism of a superconductor, called the Meissner effect. These two physical properties are independent and equally important properties of a superconductor; see, for instance, Shoenberg (1952). Ideally the measurement of either of these properties should yield the same results for the superconducting transition. However, as pointed out by Shoenberg (1947), there is a danger in determining the superconducting transition of alloys by measuring their electrical resistivity. There may be a slight inhomogeneity in the sample such that one could have a superconducting thread through an otherwise normal sample which would short-circuit the sample.

The method chosen for measuring the zero field transitions is similar to one which has been used by Webber, Reynolds, and McGuire (1949). This is an a.c. method with the sample being the core of a mutual inductance. The primary coil was made of 250 turns of copper wire and the secondary coil was made of 450 turns of copper wire each wound on Bakelite forms. A cylindrical sample 3/16" in diameter and 2" long constituted the core. A 100 cps

current was used in the primary which gave a maximum field at the center of the primary of 0.1 oer. The secondary voltage was amplified and read on an oscilloscope. With the sample in the normal state the secondary voltage was bucked out so that one would be reading from a null. When the sample becomes superconducting, its magnetic and electrical properties change markedly, causing an unbalance in the circuitry; evidenced by a secondary voltage increase.

This a.c. method is quite safe and easy to employ with the materials tested because of their high residual resistivity (being of the order of 10^{-5} ohm-cm). This means that the skin depth, discussed by Smythe (1950), of a 100 cps magnetic field would be of the order of 1.5 cm for the normal state. The samples are rods approximately 0.47 cm in diameter, hence this field will quite easily penetrate the sample when it is in the normal state. As the skin depth for the sample in the superconducting state is very small, being of the order of 10^{-5} cm, see London (1950), a large change in the secondary voltage will be observed at the transition.

For two alloys (the 80 per cent lanthanum and 20 per cent lutetium alloy, and the 95 per cent lanthanum and 5 per cent ytterbium alloy) the superconducting transition was observed both by this a.c. method and by means of the electrical resistivity as shown in later figures.

It is of interest to carefully note the character of these curves. One may observe that the first evidence of superconductivity as determined by the a.c. method commences just as the electrical resistivity vanishes. This seems to always be the case, so this point was taken as the transition temperature of the substance investigated. More justification for choosing this point is based on the work of Cook, Zemansky, and Boorse (1950) on the superconductivity of columbium.

The critical field work was performed using a d.c. method similar to that used by Keeley and Mendelsohn (1936). The secondary coil used for the a.c. work was used for the pick-up coil and was connected to a ballistic galvanometer. A solenoid, capable of producing fields to 1500 oer was used to produce a longitudinal magnetic field. The technique was to vary the magnetic field abruptly in steps, both for increasing and for decreasing fields, and measure the corresponding deflection of the ballistic galvanometer. The deflection of the galvanometer is proportional to the flux change within the pick-up coil. When the sample is in the normal state it is weakly paramagnetic; when the sample is in the superconducting state it is perfectly diamagnetic. This means that the galvanometer deflection per change in field will be quite different for these two cases. The actual sensitivities are

0.022 cm/oer for the sample in the superconducting state and 0.040 cm/oer for the sample in the normal state.

Tin was studied in liquid helium by the d.c. method and good agreement was found between this and the work of Lock, Pippard, and Shoenberg (1951). Lead was also studied and good agreement with the work of Daunt and Mendelsohn (1937) was observed when sufficient care was taken. It was found that sudden changes in the applied magnetic field of a few hundred gauss would cause heating of the sample and holder by eddy currents sufficient to raise its temperature 0.1 degree. Hence it was necessary to wait a few minutes between changes for thermal equilibrium to be restored. The tin and lead samples were not studied by the a.c. method because of the lack of sensitivity of this apparatus for samples with electrical resistivities as low as these elements have. The penetration depth of a 100 cps magnetic field for these samples would be approximately 0.3 mm as contrasted with the corresponding value of 1.5 cm for the rare earths.

For temperatures less than 4°K transition curves which were obtained with the sample in the bath were compared with the corresponding curves obtained by maintaining the bath temperature at some fixed low value and using the technique described in the following section to vary the temperature. Good agreement was found between these methods.

These tests are measures of the accuracy of the equipment which was found to be acceptable. The good reproducibility of the data taken would further indicate that the precision of the measurements taken is within the limits stated in the following section, namely that transition temperatures near 6°K are known to 0.05 degree and those at lower temperatures somewhat better.

Temperature Measurement and Control

A metal cryostat of the type described by Henry and Dolecek (1950) was used for this work. This had a leak rate of about 30 cubic cm of liquid helium per hour.

The temperature region of 1.3°K to 4.2°K can be quite easily obtained by pumping on liquid helium. A vapor pressure thermometer, based on the 1955 Agreed Scale, was employed to measure bath temperatures in this region. The temperature sensing part of the thermometer was a 7 mm Pyrex tube, sealed at the lower end, and located well in the bath. A small amount of helium was condensed in this tube and its vapor pressure measured. For temperatures between 2.2°K and 4.2°K pressures were measured with a mercury manometer, and for pressures corresponding to temperatures less than 2.2°K a butyl phthalate manometer was used.

Temperatures above 4.2°K are not easy to maintain and measure. Figure 1 shows the apparatus used for obtaining temperatures in this region. A small amount of helium

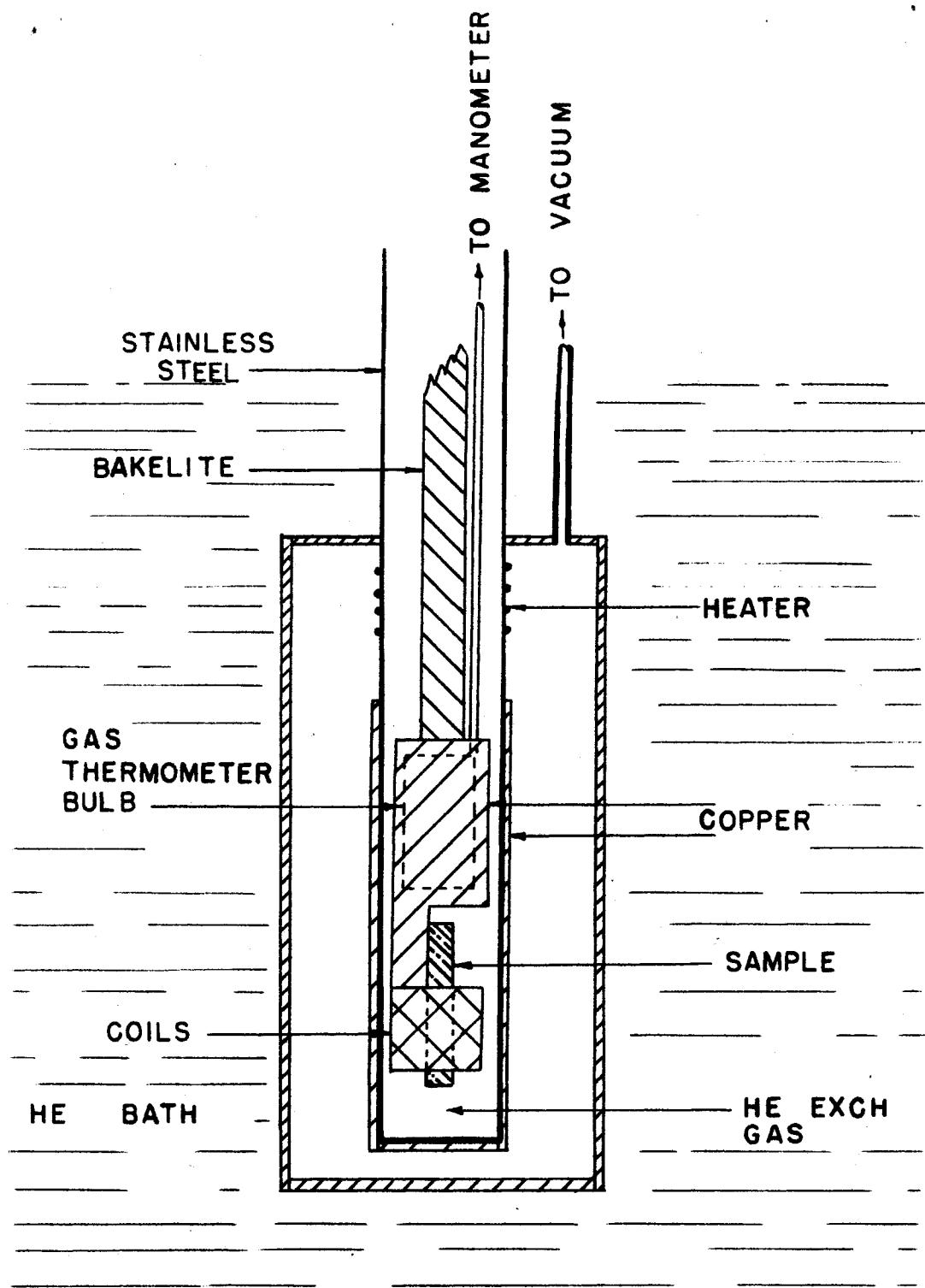


Figure 1. Apparatus for temperature control.

exchange gas in the central chamber at a pressure of approximately 50 microns allows the sample and its holder to be in thermal equilibrium with the isothermal heavy copper wall of this chamber. This chamber is in a vacuum so the only thermal path is down the support tube of "super-nickel", chosen because of its low thermal conductivity. Power to the heater was varied to obtain the desired temperatures. A power of approximately 0.01 w is necessary to maintain a sample temperature 3 degrees above the bath temperature.

Temperatures above 4.2°K were measured by a gas thermometer of the type described by Woodcock (1938). This is approximately a constant volume gas thermometer, but nevertheless is quite different. It has a low temperature bulb of volume 3.8 cm³ and an external volume of 80 cm³ connected by 75 cm of 0.05 cm I.D. stainless steel tubing which is vacuum jacketed to assure the same temperature distribution along it at all times. The relation between the temperature and pressure is

$$\frac{1}{T} = \frac{nR}{V_1} - \frac{1}{P} - \frac{A}{26T_1V_1} - \frac{P}{V_1T_1} - \frac{V_2}{V_1T_1}$$

where n is the no. of moles of helium gas

R is the gas constant

V₁ is the external volume

A is the cross-sectional area of the manometer

δ is the density of the oil in the manometer

T_1 is the room temperature

V_2 is the volume of the thermometer bulb

T is the temperature of the thermometer bulb

P is the pressure of the helium gas within the thermometer

This equation is based on certain assumptions which may be shown to be valid. For example, the perfect gas law is used. An examination of the virial equation for helium (see, for instance, Keesom (1942)), under the conditions of this experiment (pressures of the order of 2 cm mercury were used) shows the validity of this assumption. According to the work of Roberts and Sydoriak (1956) thermomolecular pressure difference may also be neglected for this case. The room temperature was assumed to be constant. A change in room temperature of 4 centigrade degrees would result in a 0.03 degree error for temperatures near 6°K, where the error would be the greatest.

The term $\frac{A}{26T_1V_1} P$ is the correction to the room temperature volume as a consequence of the change in liquid level of the manometer and is calculated from known quantities. This term is important only at the higher temperatures, being only about 0.02 degrees at 6°K and negligible at 4°K. The term $\frac{V_2}{V_1T_1}$ was determined by a calibration in the temperature range 1.3°K to 4.2°K in the following

manner; assuming the bath and the sample holder to be at the same temperature, with no heat supplied to the heater, the bath temperature and the gas thermometer pressure were measured. This was repeated for several different conditions and the mean value of the constant determined. It was found to have the value $0.069 \pm .001 \text{ deg}^{-1}$. It was necessary to recharge the thermometer for each run, so each succeeding calibration consisted merely of determining one point. The equation was then used to determine extrapolated temperatures. It is believed that temperatures near 6°K can be read with an accuracy of 0.05 deg and somewhat better for lower temperatures. The reproducibility of the data seems to verify this conclusion.

X-ray Technique

Since the superconducting transition temperature for lanthanum depends on its crystal structure, according to the work of Ziegler, Young, and Floyd (1953), it is very necessary to know the crystal structure of the polycrystalline samples studied. The technique chosen was to cut a small piece of metal from the sample and to file it into the shape of a small needle, perhaps 0.5 mm in diameter by 3 mm long. Since these alloys oxidize readily in air, the samples were enclosed in Pyrex capillaries which were evacuated and sealed off. The x-ray pictures were taken with a Debye-Scherrer powder camera.

It was found that filing definitely causes a structure change in pure lanthanum, in confirmation of observations by Ziegler, Young, and Floyd (1953). The more stable room temperature structure for lanthanum was the hexagonal close-packed structure with the layer stacking sequence being ABAC... instead of the usual ABAB... which means a c_0 axis double the normal value, as reported by Herrmann (1955). One could start with pure face-centered cubic lanthanum, prepare an x-ray sample in the way described, and discover that x-rays would reveal only the double c_0 hexagonal close-packed structure. The same result was noted with the 95 per cent lanthanum and 5 per cent yttrium alloy. Therefore the x-ray samples were given the same heat treatment as the samples used for the superconductivity measurements and were then assumed to have the same structure.

Another necessary assumption was that the structure did not undergo any change when the samples were cooled to 4°K. This seems to be a reasonable assumption for pure lanthanum according to the work of James, Legvold, and Spedding (1952) and Parkinson, Simon, and Spedding (1951) who report no anomaly below room temperature. Also Ziegler, Young, and Floyd (1953) reported that low temperature cycling had no observed effect on the crystal structure of lanthanum. It seems quite plausible to make the same assumption for the alloys examined.

MATERIALS TESTED

Preparation

The chemical similarity of yttrium and the elements of the lanthanide series has made the separation of these elements a difficult problem. This has been accomplished by Spedding and Powell (1954) using an ion-exchange method. The development of techniques for preparing the pure metals has been accomplished by Spedding and Daane (1954). The metals were then cast in tantalum crucibles. The alloys were prepared by melting together the proper amounts of each component. Following this the samples were turned down to the desired size which was a rod 3/16" in diameter by 2" long.

Purity

A spectrographic analysis of the samples investigated revealed very little metal ion impurity. The effect of the purity of a sample on its superconducting transition temperature will be discussed in a later section.

Two samples of pure lanthanum were used for this investigation. The first sample, designated hereafter in the report as lanthanum A, contained perhaps 0.01 per cent silicon and aluminum with just traces of calcium and copper. The second sample, designated hereafter as Lanthanum I,

contained perhaps 0.01 per cent calcium and copper with just a trace of silicon.

Three lanthanum-yttrium alloys were studied in this investigation. The alloy containing 95 per cent lanthanum and 5 per cent yttrium by atoms was found to contain less than 0.05 per cent aluminum, perhaps 0.01 per cent calcium and copper, and just a trace of silicon. The alloy containing 85 per cent lanthanum and 15 per cent yttrium by atoms was found to contain less than 0.05 per cent aluminum, perhaps 0.01 per cent beryllium, calcium, and copper, and just a trace of silicon. The alloy containing 60 per cent lanthanum and 40 per cent yttrium by atoms contained perhaps 0.01 per cent aluminum, calcium, and copper with just a trace of silicon.

The alloy containing 80 per cent lanthanum and 20 per cent lutetium by atoms was found to contain 0.01 per cent calcium with just traces of silicon and copper.

The analyses for the alloy containing 64 per cent lanthanum and 36 per cent lutetium and the alloy containing 95 per cent lanthanum and 5 per cent ytterbium unfortunately were not completed at the time of writing and could not be included.

Structure

Lanthanum

Pure lanthanum was found to exist in two crystalline

forms. Face-centered cubic lanthanum, which was found to be energetically more favorable at higher temperatures, in agreement with Ziegler, Young, and Floyd (1953), was found to have a lattice parameter of $a_0 = 5.304 \pm .006 \text{ \AA}$. The other structure found for pure lanthanum was hexagonal close-packed with the layer stacking sequence being ABAC..., instead of the usual ABAB..., in agreement with Herrmann (1955). This means that the c_0 axis is twice its normal size. This structure was found to have the lattice parameters $a_0 = 3.768 \pm .013 \text{ \AA}$ and $c_0 = 12.135 \pm .033 \text{ \AA}$.

Lanthanum-Yttrium

The sample containing 95 per cent lanthanum and 5 per cent yttrium by atoms was also found to exist in either of two crystalline forms. Again the face-centered cubic seemed to be the stable phase at high temperatures. This structure was found to have the lattice parameter $a_0 = 5.295 \pm .007 \text{ \AA}$. The same hexagonal structure as found in the case of lanthanum was again observed for this alloy; that is, the hexagonal close-packed structure with a double c_0 axis. The lattice parameters for this structure as measured were $a_0 = 3.753 \pm .006 \text{ \AA}$ and $c_0 = 12.131 \pm .022 \text{ \AA}$.

The alloy containing 85 per cent lanthanum and 15 per cent yttrium by atoms was found to have the hexagonal structure with the double c_0 axis. The lattice parameters

for this structure were $a_0 = 3.744 \pm .008\text{\AA}$ and $c_0 = 12.079 \pm .021\text{\AA}$.

The alloy containing 75 per cent lanthanum and 25 per cent yttrium by atoms appeared to have this same hexagonal structure with the double c_0 axis. The lattice parameters for this structure were $a_0 = 3.726 \pm .004\text{\AA}$ and $c_0 = 12.022 \pm .044\text{\AA}$.

The alloy containing 60 per cent lanthanum and 40 per cent yttrium by atoms also had this same hexagonal structure with the double c_0 axis. The lattice parameters measured for this structure were $a_0 = 3.715 \pm .012\text{\AA}$ and $c_0 = 11.955 \pm .025\text{\AA}$.

The lattice parameters for the hexagonal structure with the double c_0 axis as a function of the yttrium concentration in lanthanum is shown in Figure 2. These plots are evidently straight lines. The solid curves drawn in were obtained by using the atomic volumes of lanthanum and yttrium and calculating from these what the volumes for the various alloys would be. The values for the lattice parameters, the ratio of the lattice parameters, and the volume per atom are shown in Table 1 for these alloys. The values of the lattice constants reported by Herrmann (1955) for lanthanum are $a_0 = 3.770 \pm .002\text{\AA}$ and $c_0 = 12.159 \pm .008\text{\AA}$ with the hexagonal structure having the stacking sequence ABAC..., and for yttrium are $a_0 = 3.6474 \pm .0007\text{\AA}$ and $c_0 = 5.7306 \pm .0008\text{\AA}$ with the ordinary hexagonal close-

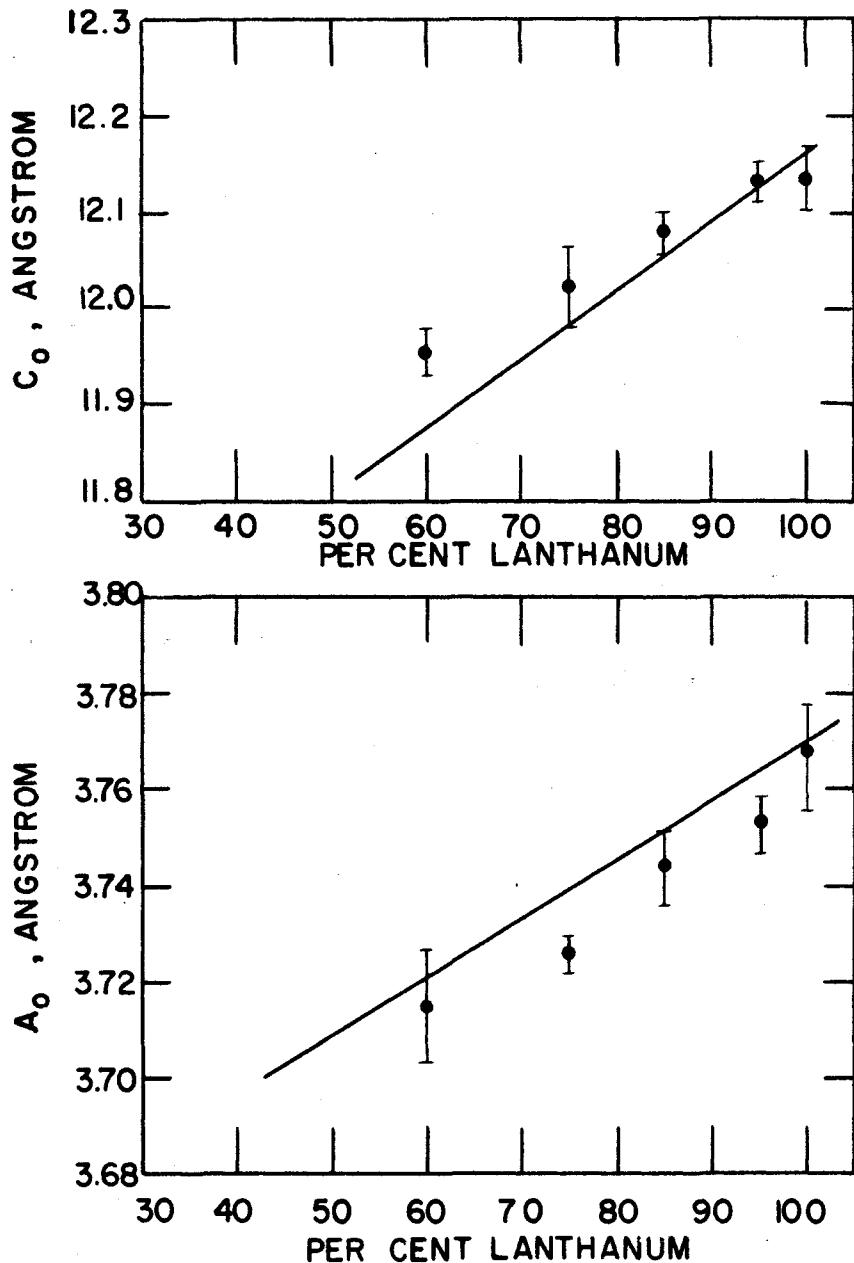


Figure 2. Hexagonal lattice parameters as a function of composition for the lanthanum-yttrium alloys. (The solid lines are the ideal curves.)

Table 1. Lattice parameters for the lanthanum-yttrium system

Alloy	$a_o, \text{\AA}$	$c_o, \text{\AA}$	c_o/a_o	Vol/atom $\text{cm}^3 \times 10^{-24}$
100% La- 0% Y	$3.768 \pm .013$	$12.135 \pm .033$	3.22	37.4
95% La- 5% Y	$3.753 \pm .006$	$12.131 \pm .022$	3.23	37.0
85% La-15% Y	$3.744 \pm .008$	$12.079 \pm .021$	3.23	36.7
75% La-25% Y	$3.726 \pm .004$	$12.022 \pm .044$	3.23	36.1
60% La-40% Y	$3.715 \pm .012$	$11.955 \pm .025$	3.22	35.7

packed structure. The ratio c_o/a_o for lanthanum is 3.225 while a value 3.14 is found for yttrium for the ratio $2 c_o/a_o$, which is used to permit a direct comparison. Since the ideal ratio would be 3.266, the packing is more ideal for the stacking sequence ABAC... than for the stacking sequence ABAB.... It is significant that the ratio c_o/a_o for these alloys is very constant at the value for pure lanthanum and this would indicate that yttrium atoms replace lanthanum atoms in the lattice.

Lanthanum-Ytterbium

The alloy containing 95 per cent lanthanum and 5 per cent ytterbium by atoms was found to have the hexagonal close-packed structure with the layer stacking sequence ABAC... instead of the usual ABAB.... The lattice parameters for this structure were $a_o = 3.767 \pm .017 \text{\AA}$ and $c_o = 12.158 \pm .045 \text{\AA}$.

Lanthanum-Lutetium

The alloy containing 80 per cent lanthanum and 20 per cent lutetium by atoms was found to have the hexagonal close-packed structure with the layer stacking sequence ABAC... instead of the usual ABAB.... The lattice parameters measured for this structure were $a_o = 3.719 \pm .005 \text{ \AA}$ and $c_o = 11.980 \pm .023 \text{ \AA}$.

The alloy containing 64 per cent lanthanum and 36 per cent lutetium by atoms seemed to have this same hexagonal structure. The lattice parameters measured for this structure were $a_o = 3.67 \pm .03 \text{ \AA}$ and $c_o = 11.85 \pm .05 \text{ \AA}$. Difficulty in the casting process made the percentages of lanthanum and lutetium in this alloy somewhat uncertain. The values for the lattice parameters, the ratio of the lattice parameters, and the volume per atom is shown in Table 2 for these alloys.

Table 2. Lattice parameters for the lanthanum-lutetium system

Alloy	$a_o, \text{\AA}$	$c_o, \text{\AA}$	c_o/a_o	Vol/atom $\text{cm}^3 \times 10^{-24}$
100% La- 0% Lu	$3.768 \pm .013$	$12.135 \pm .003$	3.22	37.4
80% La-20% Lu	$3.718 \pm .005$	$11.980 \pm .023$	3.22	35.9
64% La-36% Lu	$3.67 \pm .03$	$11.85 \pm .05$	3.23	34.6

The values for the lattice constants reported by Herrmann (1955) for lutetium are $a_0 = 3.5031 \pm .0004$ and $c_0 = 5.5509 \pm .0004$ with the ordinary hexagonal close-packed structure. The ratio c_0/a_0 for lanthanum is 3.225 while a value 3.17 is found for lutetium for the ratio $2 c_0/a_0$, which is used to permit a direct comparison. The packing is again more ideal for the stacking sequence ABAC... than for the stacking sequence ABAB..., since the ideal ratio would be 3.266. The constancy of this ratio for these alloys would indicate that lutetium atoms replace lanthanum atoms in the lattice.

RESULTS

Lanthanum

A lanthanum sample, designated as lanthanum I, was run as received. This sample had been cast and turned down to the proper size. The curve of the secondary voltage vs. temperature is shown in Figure 3. One may note several interesting characteristics of this curve. First we may note that it has a transition temperature of 5.8°K . A second interesting aspect is the evidence of a second transition near 5.0°K , evidently corresponding to a different structure. A third characteristic that should be noted is the great broadness of the transitions, which evidently indicates a strained sample.

Barson, Legvold, and Spedding (1957) note a phase transition in lanthanum near 300°C . Above this temperature the stable crystal structure should be face-centered cubic, according to Ziegler, Floyd, and Young (1953). The sample was then annealed at 400°C for $4\frac{1}{2}$ days and quenched in order to keep the structure which is stable at higher temperatures. X-ray analysis of this sample, designated as lanthanum II, revealed its structure to be face-centered cubic. The curve of the secondary voltage vs. temperature is shown in Figure 3. This curve is markedly different from the curve obtained before the sample was annealed. The sample now has a superconducting transition at 5.9°K ,

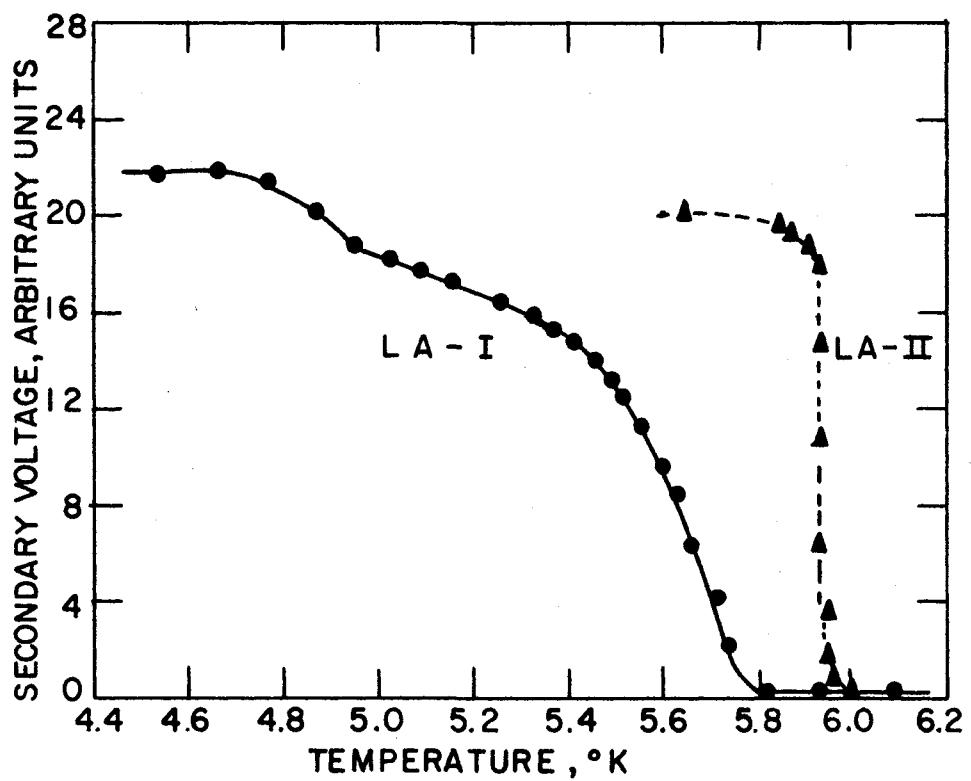


Figure 3. Secondary voltage as a function of temperature for lanthanum I and lanthanum II.

slightly higher than previously, and is now quite sharp, having a width of approximately 0.1 degree. There is no evidence for the 5.0°K transition for this sample.

The sharpness of this transition indicated a relatively unstrained sample and suggested that it would be possible to do critical field studies for this sample. Hence it was studied with the d.c. method described earlier. The galvanometer deflections vs. the applied fields are shown for various isotherms in Figures 4-6. Note that penetration of the magnetic field commences at a rather well-defined value. However, one must apply very strong fields before the sample is entirely in the normal state. It is believed, along with Jackson and Preston-Thomas (1950), Love (1953), and Wexler and Corak (1952), that the penetration fields are much nearer the equilibrium fields than are the completion fields. This point will be discussed more completely in a later section. A plot of the penetration fields vs. transition temperatures is shown in Figure 7. The initial slope of this curve, that is $\frac{dH}{dT} \Big|_{T=T_c}$, was found to be 550 oer/deg. The transition temperature as determined by extrapolation of H_c vs. T^2 , shown in Figure 7, to zero field, is 5.82°K. The difference between this value and the corresponding value for the a.c. measurements is not understood. The difference in specific heats of the superconducting and the normal states is calculated by use of Rutger's formula

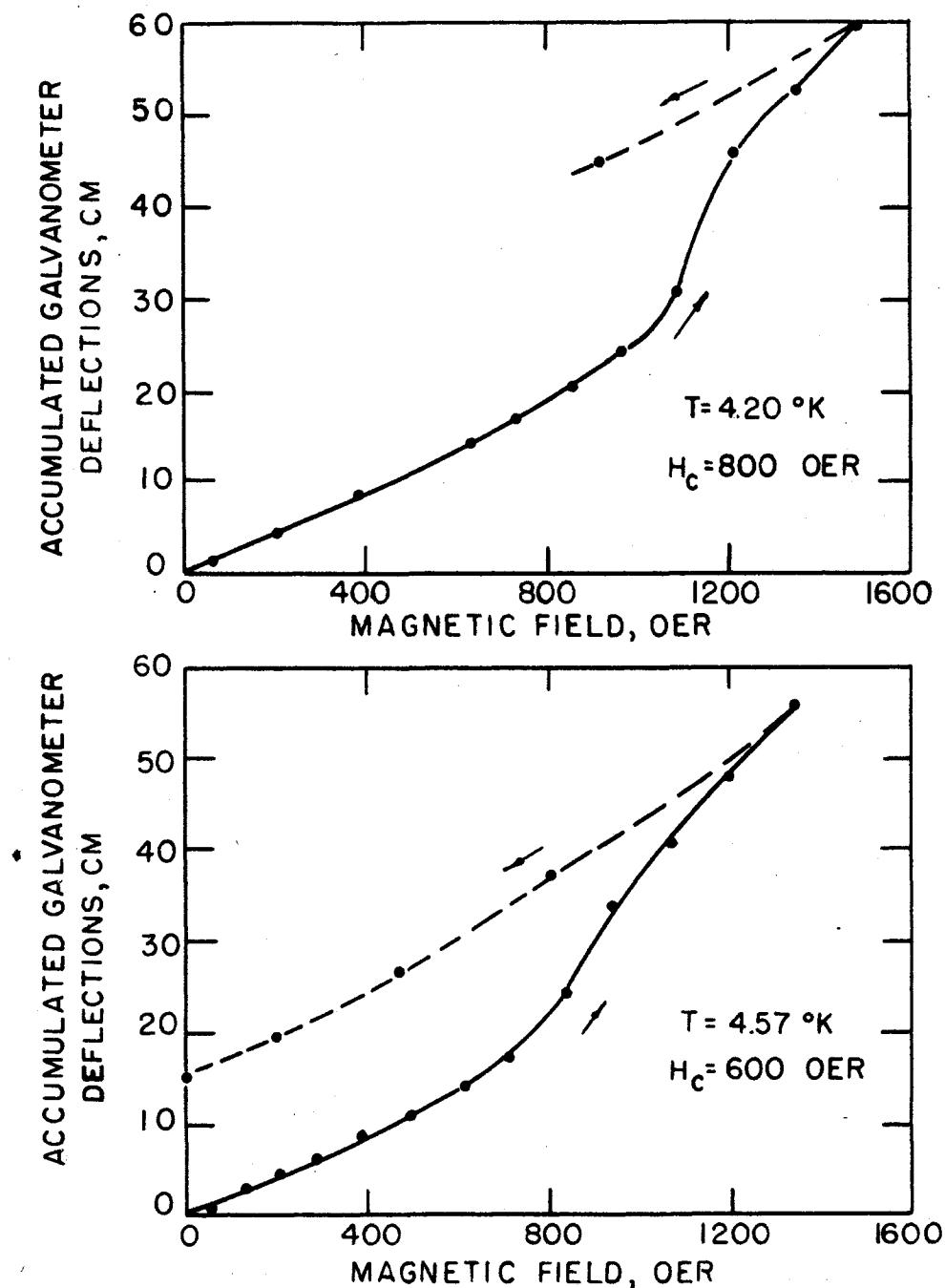


Figure 4. Accumulated glavanometer deflections as a function of longitudinal magnetic field for lanthanum II at constant temperature. (The solid curves are for increasing fields and the broken curves are for decreasing fields.)

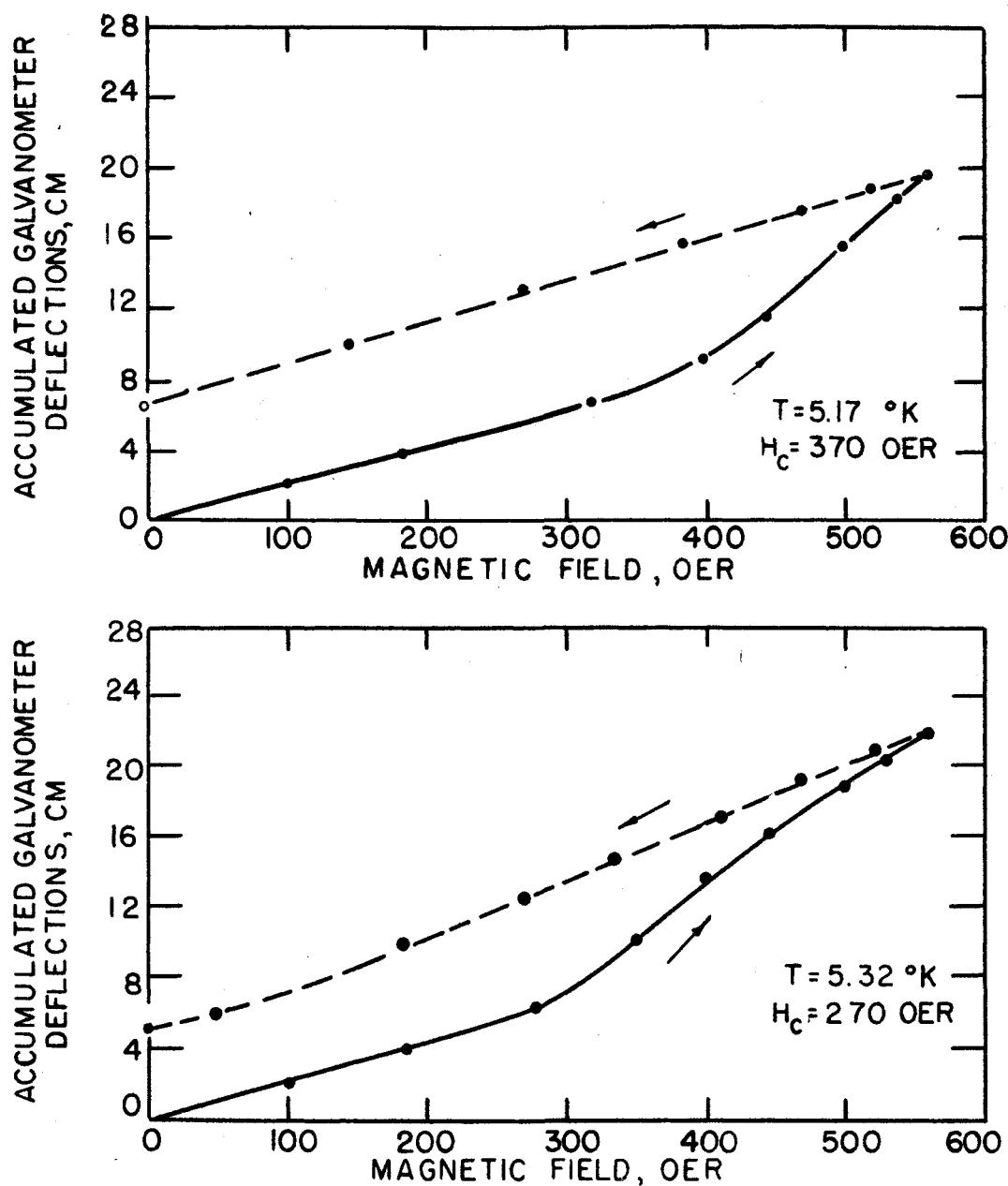


Figure 5. Accumulated galvanometer deflections as a function of the longitudinal magnetic field for lanthanum II at constant temperature. (The solid curves are for increasing fields and the broken curves are for decreasing fields.)

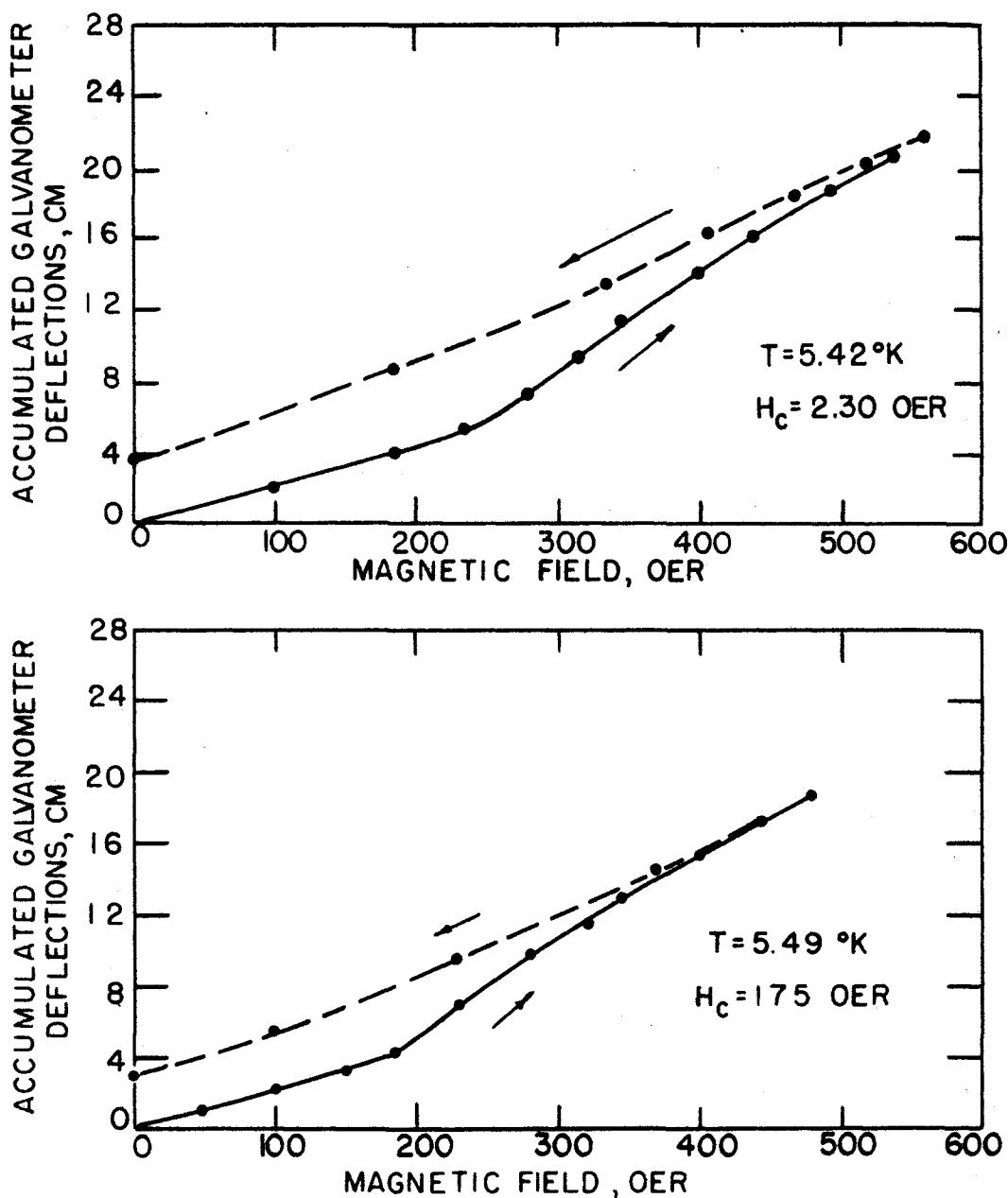


Figure 6. Accumulated galvanometer deflections as a function of longitudinal magnetic field for lanthanum II at constant temperature. (The solid curves are for increasing fields and the broken curves are for decreasing fields.)

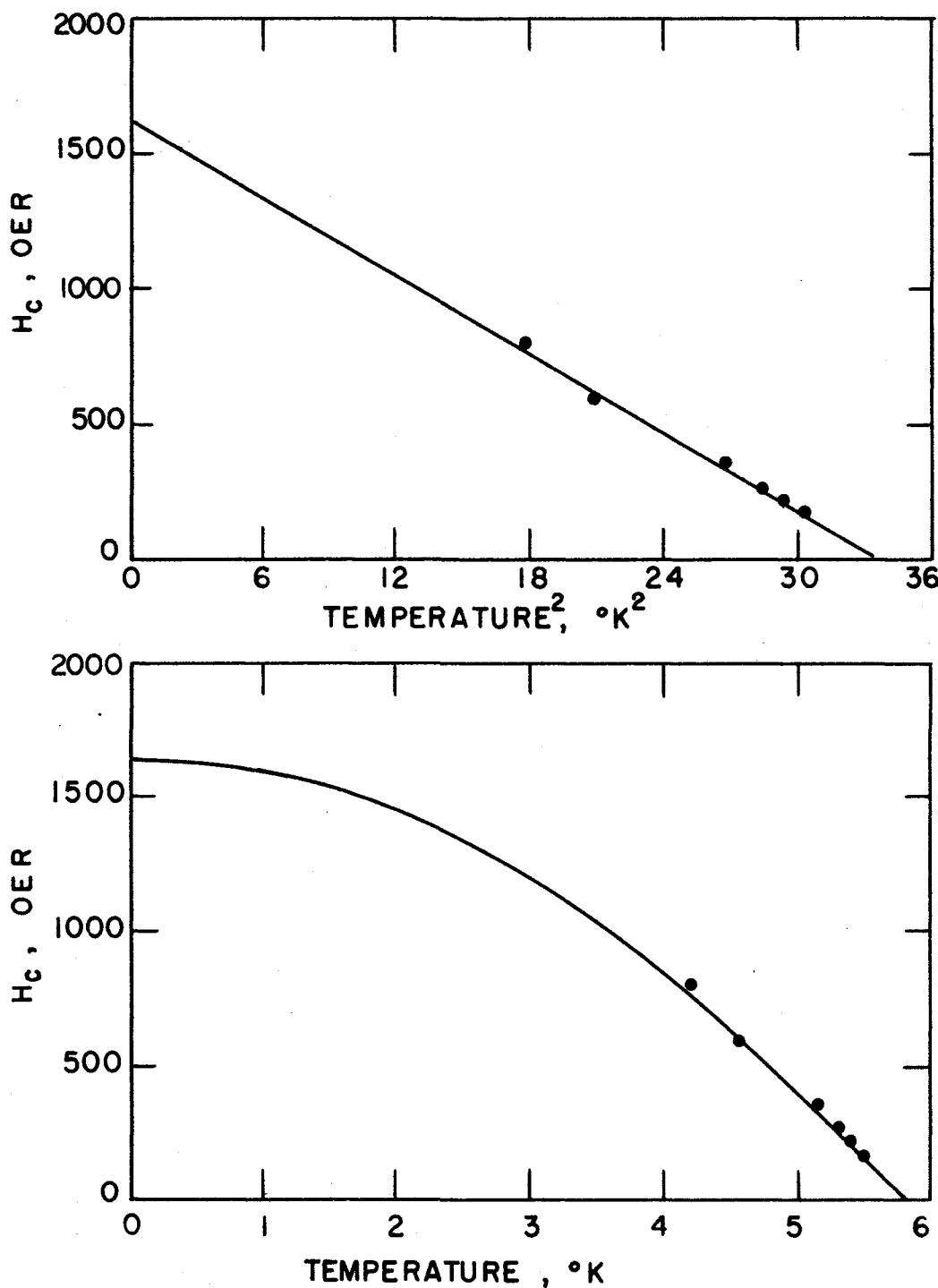


Figure 7. Critical magnetic field as a function of temperature and temperature squared.

$$C_s - C_n = \frac{VT_c}{4\pi} \left(\frac{dH_c}{dT} \right)^2 \Big|_{T = T_c}$$

where V is the specific volume, T_c is the superconducting transition temperature in the absence of an applied field, H_c is the critical magnetic field, and T is the temperature, to be approximately 0.103 cal./mole deg. The only published specific heat data for lanthanum is the work of Parkinson, Simon, and Spedding (1951) who found $\Delta C_p = 0.0139$ cal./mole deg. with a transition temperature of $4.37^\circ K$.

This sample was then run again by the a.c. method. The transition temperature was now found to be $5.9^\circ K$, which is exactly the same as was previously determined by this method.

Another pure sample of lanthanum (lanthanum A) was run as received. This sample also had been cast and turned down to the proper size. A plot of the secondary voltage vs. temperature is shown in Figure 8. This curve is very similar to the virgin curve for the other sample of pure lanthanum. It shows one transition at $5.8^\circ K$ and another at $5.0^\circ K$.

Since the hexagonal structure with a double c_0 axis, which is more stable at lower temperatures, is believed to be responsible for the lower superconducting transition temperature, this sample was annealed at $200^\circ C$ for 5 days. This temperature should be the highest temperature for

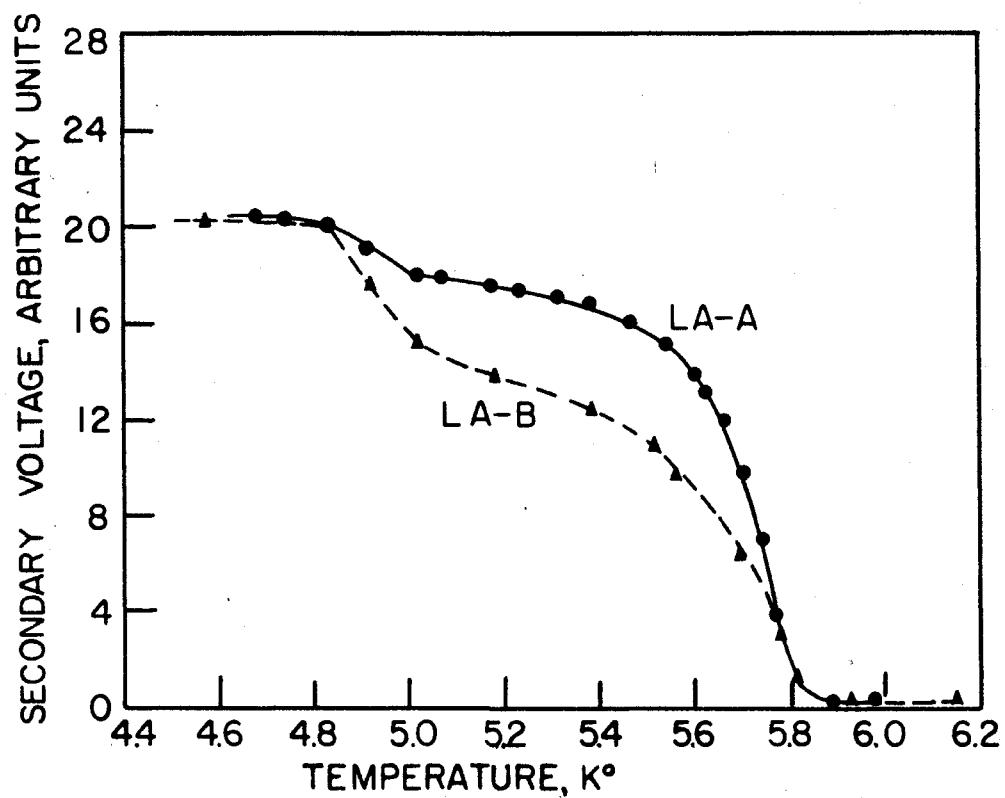


Figure 8. Secondary voltage as a function of temperature for lanthanum A and lanthanum B.

which this structure is the most stable. (Cf. Barson, Legvold, and Spedding (1957).) A plot of the secondary voltage vs. temperature is shown in Figure 8. Note that the transition at 5.0°K has definitely been enhanced and the higher temperature transition has been correspondingly diminished in magnitude. The higher transition temperature seems to be slightly higher after the annealing; however this difference may not be real.

We can therefore quite definitely say that face-centered cubic lanthanum has a higher superconducting transition temperature, perhaps 5.9°K, than does the hexagonal structure described in this paper, which seems to show a transition near 5.0°K. The significance of this result and the critical field work will be discussed in a later section.

Lanthanum-Yttrium

Pure yttrium does not become superconducting above 0.10°K according to Goodman (1951). This fact is quite puzzling in the sense that nearly all empirical relations predict, or at least indicate, that yttrium should be a superconductor. It is an element similar to lanthanum, having three conduction electrons per atom as lanthanum does. Its ionic radius is slightly smaller than that of lanthanum and its atomic mass is somewhat less.

As has been mentioned earlier, superconducting transition temperatures apparently depend, among other things, upon the number of conduction electrons per atom, the atomic volume, and the atomic mass. By alloying yttrium with lanthanum one is able to maintain the same number of conduction electrons per atom while varying the volume and the mass. Because of the similarity of these two elements, it was felt that it would be possible to have good solid solutions over a wide range of compositions.

The sample containing 60 per cent lanthanum and 40 per cent yttrium by atoms had the hexagonal close-packed structure with the stacking ABAC... instead of the normal ABAB.... The secondary voltage vs. temperature for this sample is shown in Figure 9. Its transition temperature, as determined in this manner, was found to be 1.8°K. The transition had a width of 0.3 degree, which is typical of alloys.

The sample containing 75 per cent lanthanum and 25 per cent yttrium by atoms had this same structure. The plot of its secondary voltage vs. temperature is shown in Figure 10. Its transition temperature was found to be 2.6°K. The transition breadth was approximately 0.3 degree.

The sample containing 85 per cent lanthanum and 15 per cent yttrium by atoms also had this same structure.

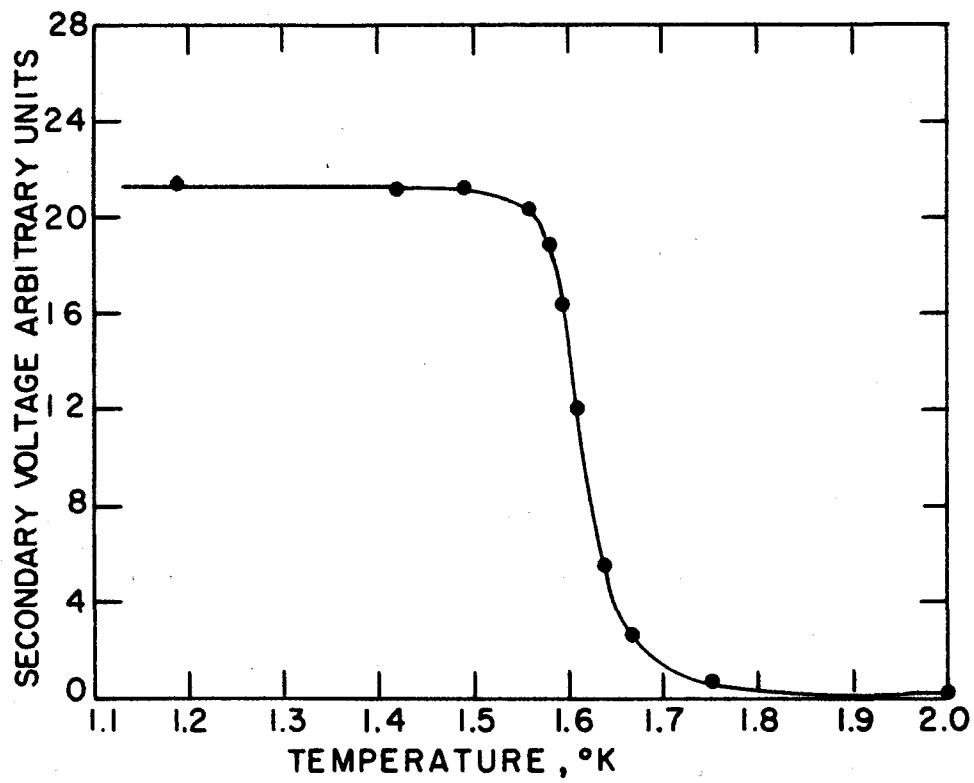


Figure 9. Secondary voltage as a function of temperature for the alloy of 60 per cent lanthanum and 40 per cent yttrium.

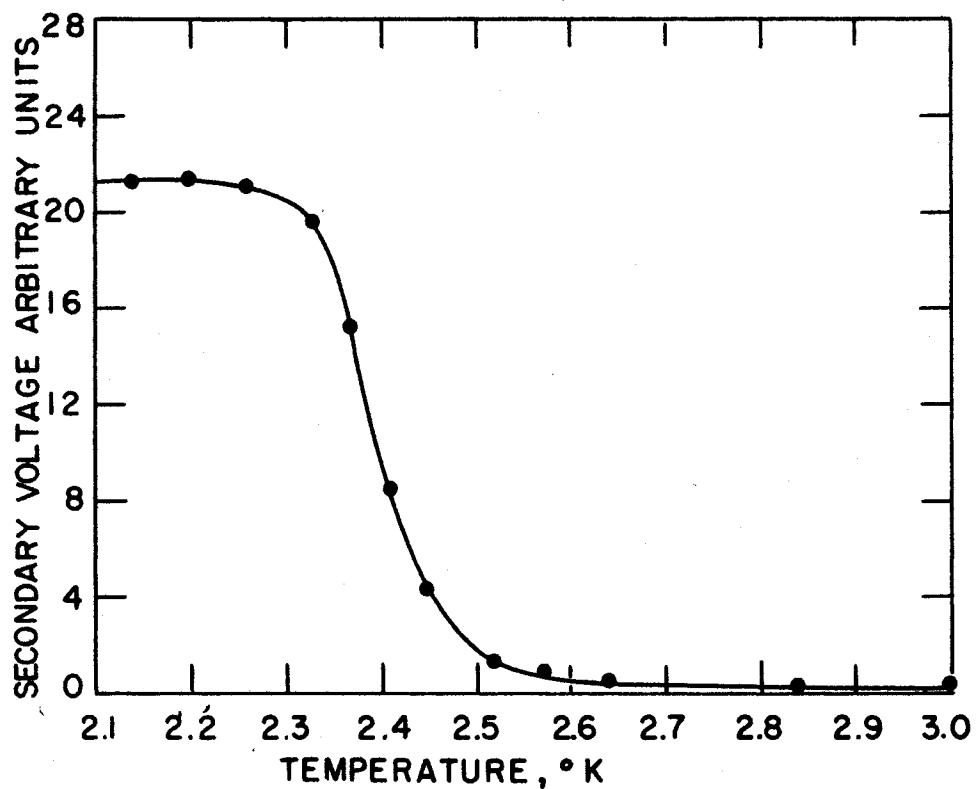


Figure 10. Secondary voltage as a function of temperature for the alloy of 75 per cent lanthanum and 25 per cent yttrium.

The secondary voltage as a function of temperature for this sample is shown in Figure 11. It had a transition temperature of 3.3°K with a transition width of approximately 0.3 degree.

The sample containing 95 per cent lanthanum and 5 per cent yttrium by atoms was found to exist in the same two crystalline forms observed for lanthanum. The secondary voltage as a function of temperature for this sample is shown in Figure 12. Its transition temperature was found to be 5.4°K , with a transition width of approximately 0.3 degree. Comparison of this transition temperature with others for the same system indicated that the observed transition was for the face-centered cubic structure. There is no evidence for a superconducting transition for the hexagonal structure. There is good evidence for a phase transition in the temperature range 400°C to 550°C , according to dilatometric measurements by Born (1957). X-ray studies after annealing at various temperatures indicate that this transition is the hexagonal-cubic one, with the cubic structure being stable at the higher temperatures. The sample was then annealed at 360°C for three weeks in an attempt to obtain enough of the hexagonal structure to enable one to observe its superconducting transition temperature. As a result of this annealing one superconducting transition was observed; that being at 5.8°K with a transition width of 0.3 degree.

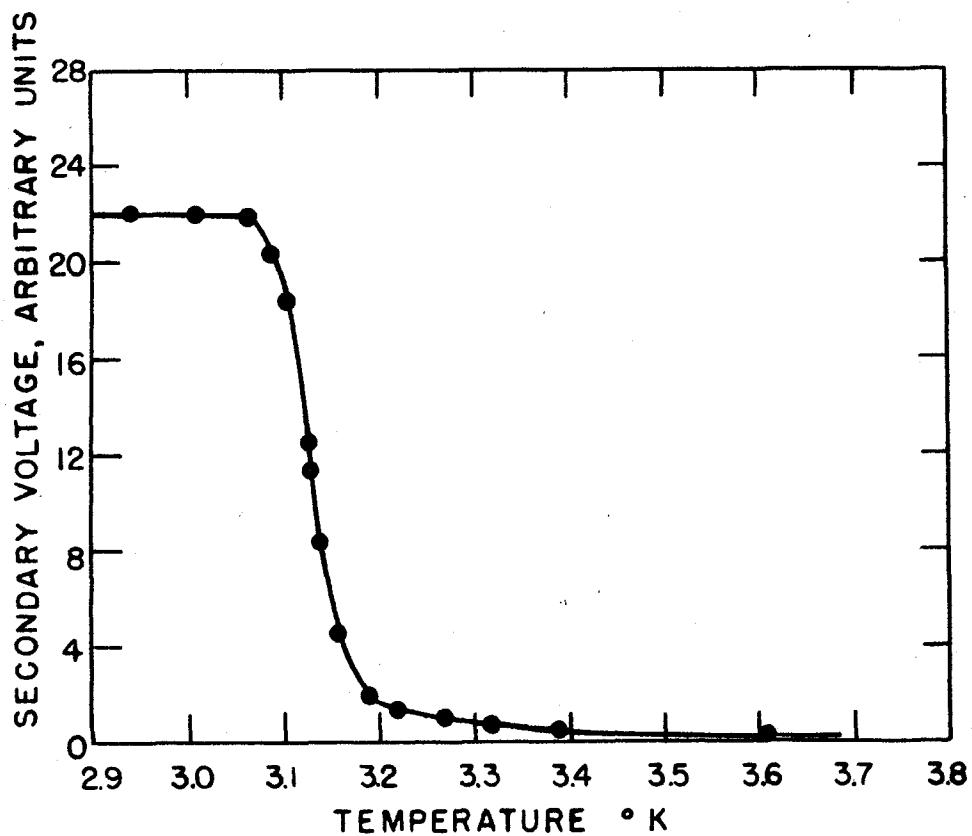


Figure 11. Secondary voltage as a function of temperature for the alloy 85 per cent lanthanum and 15 per cent yttrium.

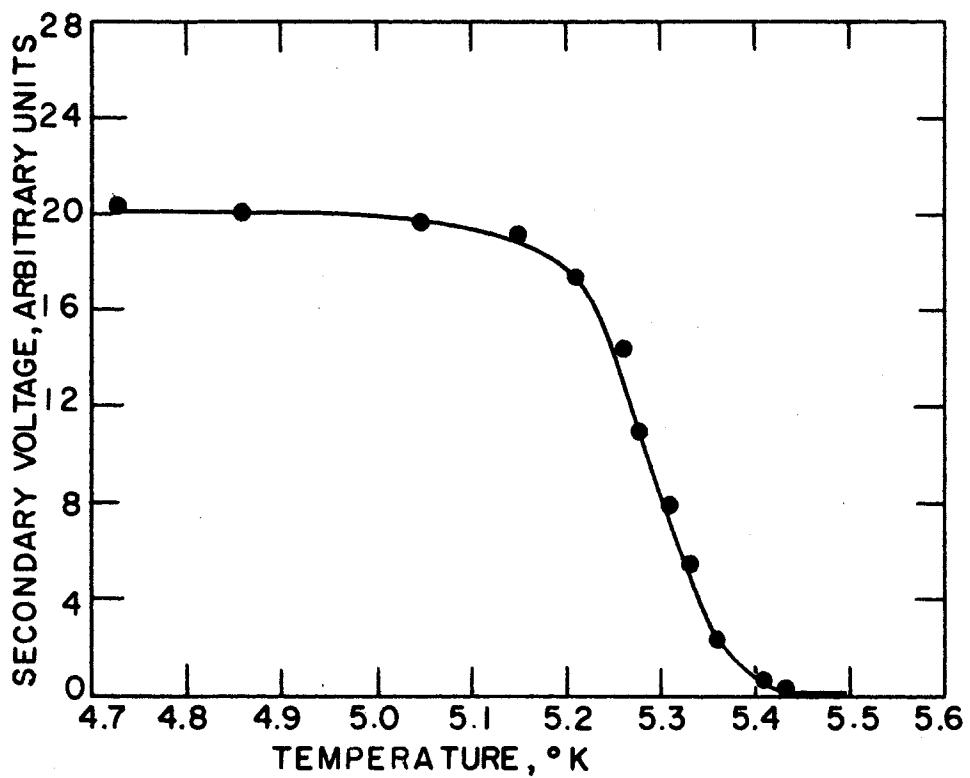


Figure 12. Secondary voltage as a function of temperature for the alloy 95 per cent lanthanum and 5 per cent yttrium.

This transition is not properly understood. One possibility is that the observed transition is for face-centered cubic lanthanum. However there is presently no evidence to corroborate this conjecture.

A plot showing the transition temperatures as a function of the composition is shown in Figure 13 for this alloy system. This curve has several interesting features. The importance that the structure has on superconductivity is indicated by the two independent curves. The curve lying on the higher temperature side represents the transition temperatures for the face-centered cubic structure. The curve lying on the lower temperature side represents the transition temperatures for the hexagonal structure which has the double c_0 axis. The transition temperature seems to decrease in a regular manner with increasing yttrium content.

It is of interest to try to determine what functional dependence the transition temperature has on the volume and mass. This may be sensible in that the crystal structure and the number of conduction electrons per atom remain constant along each curve. The volume dependence of the transition temperature was found to be V^a where $a = 25 \pm 2$.

The dependence on the mass was not sufficiently sensitive to be definitely ascertained; however an inverse dependence on the mass to some power less than, or equal to, one was used. This is the type of dependence examined by others, as we have mentioned earlier.

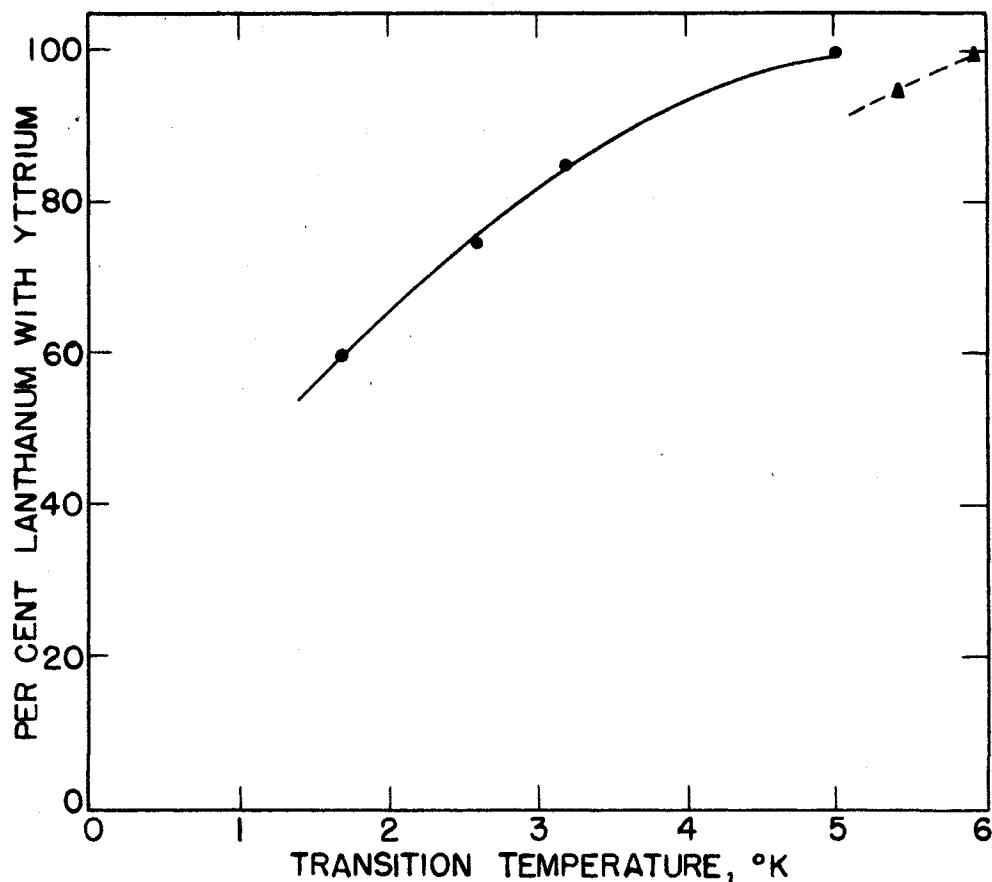


Figure 13. Transition temperatures as a function of composition for lanthanum-yttrium alloys. (The solid curve is for the hexagonal structure and the broken curve is for the cubic structure.)

Lanthanum-Ytterbium

The electrical resistivity of pure ytterbium has been examined at this laboratory down to 2.2°K with no evidence of superconductivity being observed. Ytterbium is also a member of the lanthanide series, however it is not as similar to lanthanum as lutetium is. Ytterbium is next to the last of this series and might be expected to have thirteen $4f$ electrons and three conduction electrons. However it is energetically more favorable for it to complete the $4f$ band and to have just two conduction electrons per atom. According to Herrmann (1955) ytterbium has the face-centered cubic structure with an atomic volume slightly greater than that for lanthanum.

The one alloy of this type studied contained 95 per cent lanthanum and 5 per cent ytterbium. It was found to have the hexagonal close-packed structure with the layer stacking sequence ABAC... instead of the usual ABAB.... The secondary voltage vs. temperature for this sample is shown in Figure 14. The transition temperature, as determined from this curve, was found to be 4.0°K. The transition breadth was approximately 0.2 degree.

Lanthanum-Lutetium

The electrical resistivity of pure lutetium has been examined at this laboratory down to 2.2°K with no evidence of superconductivity being observed. Lutetium is another

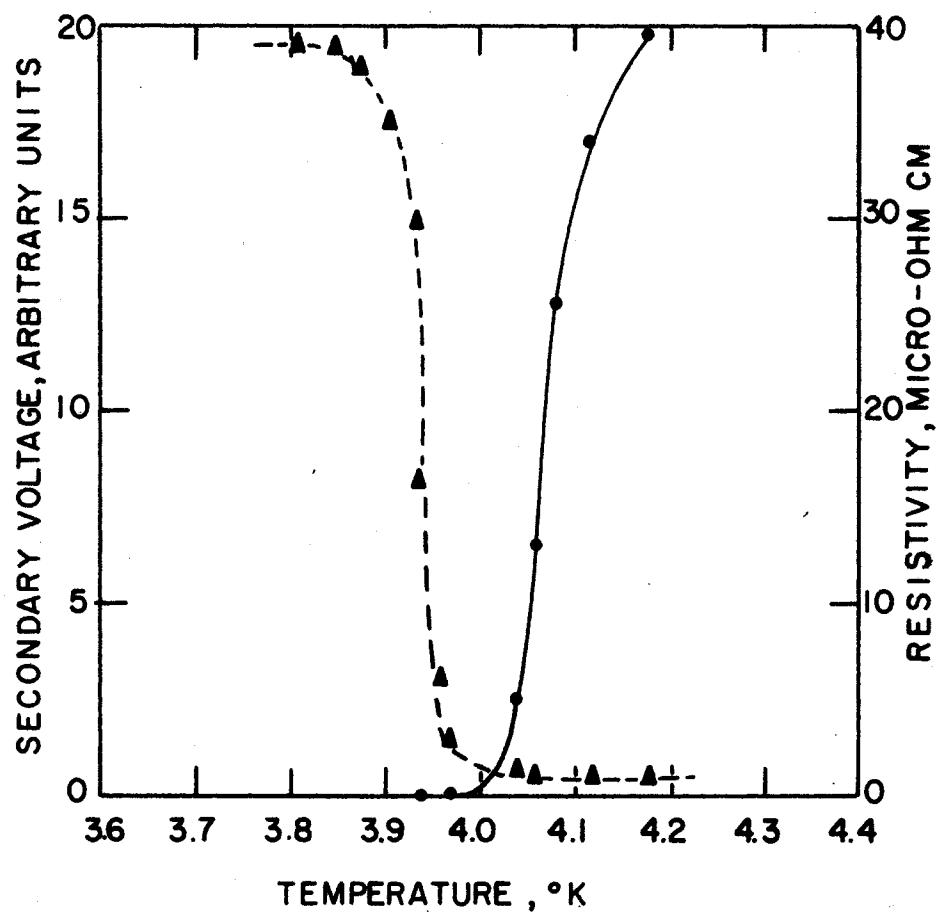


Figure 14. Secondary voltage and resistivity as a function of temperature for the alloy 95 per cent lanthanum and 5 per cent ytterbium. (The solid curve is the resistivity and the broken curve is the secondary voltage.)

element quite similar to lanthanum, having the same three conduction electrons per atom. The difference in the electron configuration of these elements lies in the 4f band which is completely empty in lanthanum and is completely filled in lutetium. Lutetium has the hexagonal close-packed structure with an atomic volume slightly less than that of either yttrium or lanthanum and an atomic mass somewhat greater than that of lanthanum. It was expected that lanthanum and lutetium would also form good solid solutions.

The sample containing 80 per cent lanthanum and 20 per cent lutetium by atoms had the hexagonal close-packed structure with the layer stacking sequence ABAC... instead of the normal ABAB.... The secondary voltage vs. temperature for this sample is shown in Figure 15. Its transition temperature, as so determined, was found to be 3.4°K . The transition width was approximately 0.3 degree.

The sample containing 64 per cent lanthanum and 36 per cent lutetium by atoms seemed to have the hexagonal close-packed structure with the layer stacking sequence ABAC... instead of the usual ABAB.... The secondary voltage vs. temperature for this sample is shown in Figure 16. Its transition temperature, as so determined, was found to be 2.0°K . The transition width was approximately 0.2 degree.

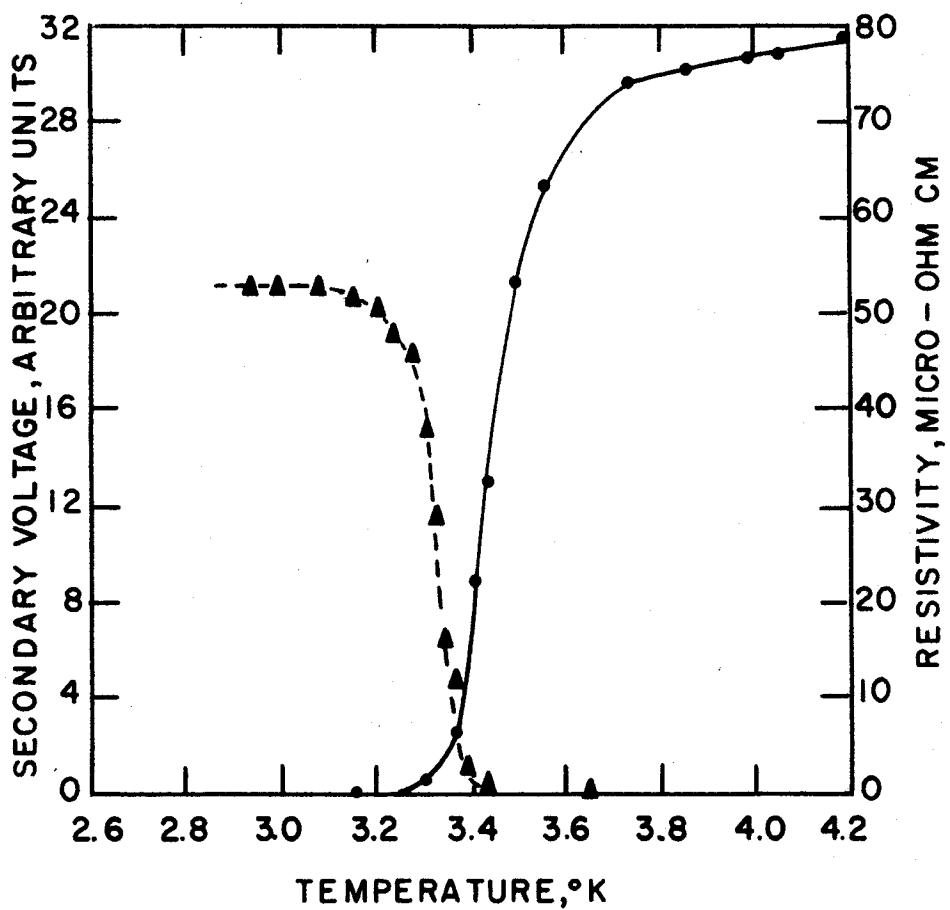


Figure 15. Secondary voltage and resistivity as a function of temperature for the alloy 80 per cent lanthanum and 20 per cent lutetium. (The solid curve is the resistivity and the broken curve is the secondary voltage.)

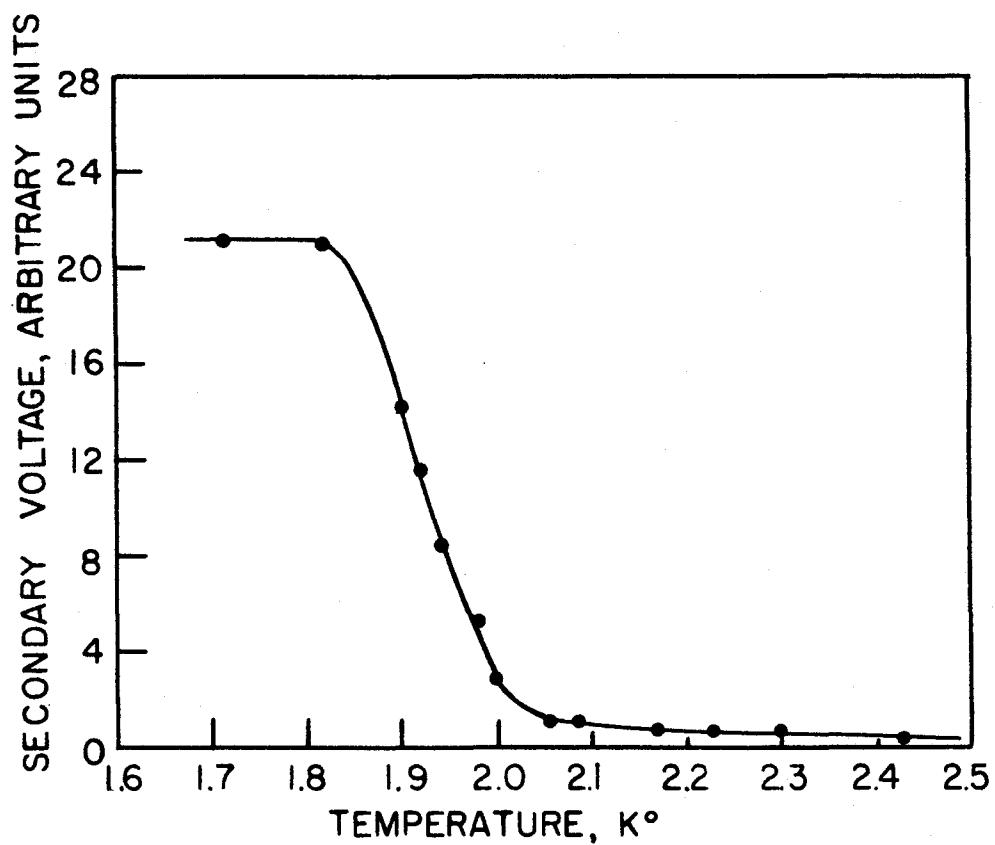


Figure 16. Secondary voltage as a function of temperature for the alloy of 64 per cent lanthanum and 36 per cent lutetium.

Summary Graph of Results

A summary of all measured transition temperatures as a function of the per cent lanthanum with yttrium, ytterbium, and lutetium is shown in Figure 17.

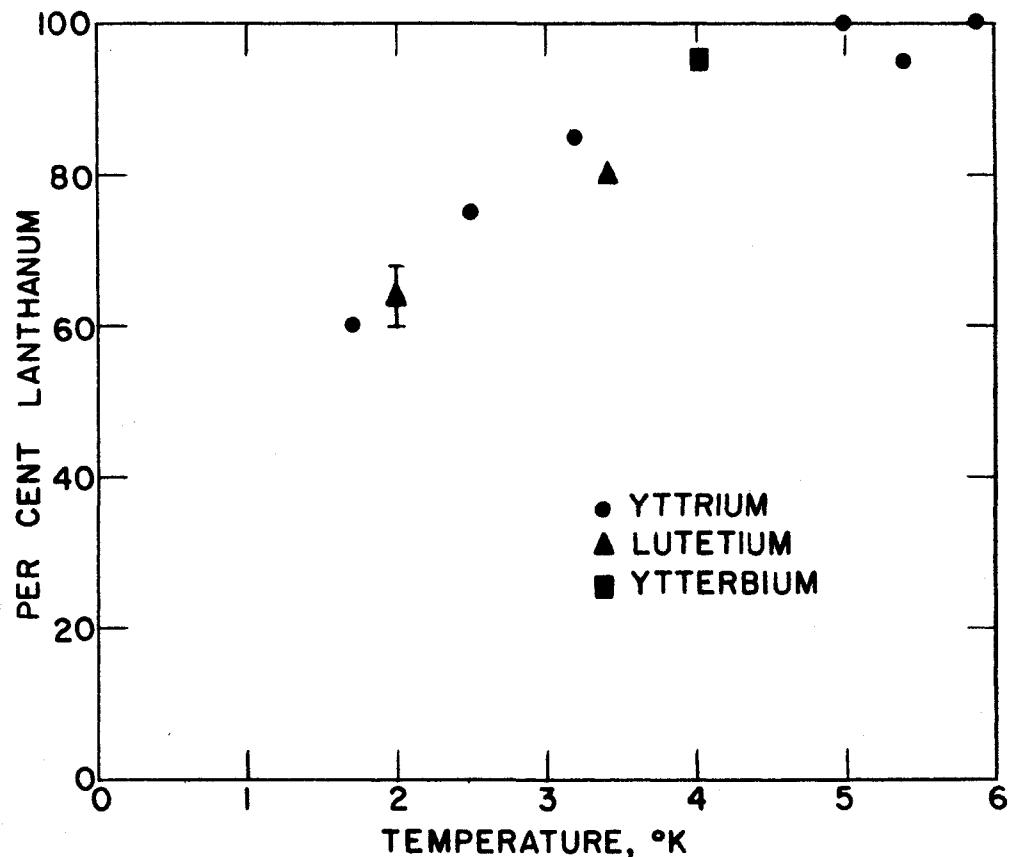


Figure 17. Transition temperatures as a function of composition.

DISCUSSION

Critical Field

The restoration of the normal state in a superconductor below the superconducting transition temperature by means of a magnetic field was first observed by Onnes (1914). However it was not until much later that the significance of this phenomenon was realized. During the early days it was thought that a superconductor was merely a perfect conductor, which would mean that the transition should be irreversible.

In 1933 Meissner and Ochsenfeld (1933) discovered the perfect diamagnetic property of a superconductor, the Meissner effect, which established the fact that the superconducting transition is reversible. This explained the success of the application of thermodynamics for a reversible transition to the superconducting transition. According to this thermodynamic treatment the superconducting and normal states are really just two phases for the substance. For temperatures below the transition temperature and in the absence of a field the superconducting state has a lower free energy than the normal state and hence is the stable state. However for a constant temperature below the transition temperature an applied magnetic field will increase the free energy of the superconducting state, the increase being proportional to the

square of the applied magnetic field. For a particular temperature there exists a certain critical field where the superconducting and normal phases are in equilibrium. This critical field increases for decreasing temperatures.

The difference in specific heats of the normal and superconducting phases is given by the Rutger's formula:

$$C_s - C_n = \frac{VT_c}{4\pi} \left(\frac{dH_c}{dT} \right)^2 T = T_c$$

as was mentioned in the section on the results of lanthanum. This equation depends only upon the reversibility of the process. The specific heat of the normal state is approximately given by $C_n/V = aT + bT^3$, where the linear term is the Sommerfeld electronic contribution and the cubic term is the Debye lattice contribution. The specific heat of the superconducting state, according to the work of Keesom and van Laer (1938), is given by $C_s/V = BT^3$, where this term is the sum of the lattice and electronic contribution. Using these expressions one may obtain further relations. The critical field as a function of temperature will be given by the equation $H_c = H_0 [1 - (T/T_c)^2]$. The coefficient of the linear term of the normal specific heat, a , will be given by $a = H_0^2 / 2\pi T_c^2$, and also we may derive a third relation, namely that $3a = (B - b)T_c^2$. The parabolic temperature dependence of the critical field

has been found to be only approximately correct (See, for instance, a summary given by Marcus and Maxwell (1953)).

Experiments seem to indicate that the superconducting transition in a magnetic field should be very sharp, since it is sharper for purer and less strained samples. However as the substance becomes more strained, the transition becomes broader and less reversible until the applicability of thermodynamics, as developed by Gorter and Casimir (1934), becomes quite questionable. When the transition is very broad, as it is for the lanthanum studied in this report, it is difficult to ascertain definitely what one should call the critical field. The initial penetration observed here is relatively sharp, however completion occurs slowly and for very large fields. Wexler and Corak (1952) and Love (1953) consider the penetration fields to be nearest the equilibrium field values. Earlier Jackson and Preston-Thomas (1950) discussed this problem and reached the same conclusion. The fields where penetration has just been completed are almost surely not the characteristic field values, as evidenced by the values they would yield for $C_s - C_n$.

The arguments of Jackson and Preston-Thomas (1950) are based on a model proposed by Mendelsohn (1935). This model supposed the superconductor to resemble a sponge, whose meshes have a much higher critical field than the matter they enclose. This inhomogeneity is presumably due

to strains of some type, either by dislocations or impurities. Hence, although most of the volume of the substance will be in the normal state for fields greater than the true characteristic critical fields, some of the substance will remain superconducting to very high fields. These meshes will form a path for an electric current, so resistivity will not be restored until one reaches very high field strengths. However this explanation is not completely satisfactory since it is very difficult to understand how the meshes can have such very high critical fields.

A more plausible explanation was proposed by Faber (1952) who suggested that certain regions of negative surface energy exist in a strained sample. This may also explain the observed behavior in a more acceptable way but will not be discussed further here.

For these reasons the penetration field values were associated with the critical field for the case of lanthanum. Lanthanum evidently also belongs to the class of hard superconductors, so-called because of their apparent high critical field values.

The alloys exhibited the wide transition breadth and irreversibility that lanthanum did to a much greater extent. Figure 18 shows the results of the ballistic method as applied to the 80 per cent lanthanum and 20 per cent lutetium alloy, which is representative of the alloys. It

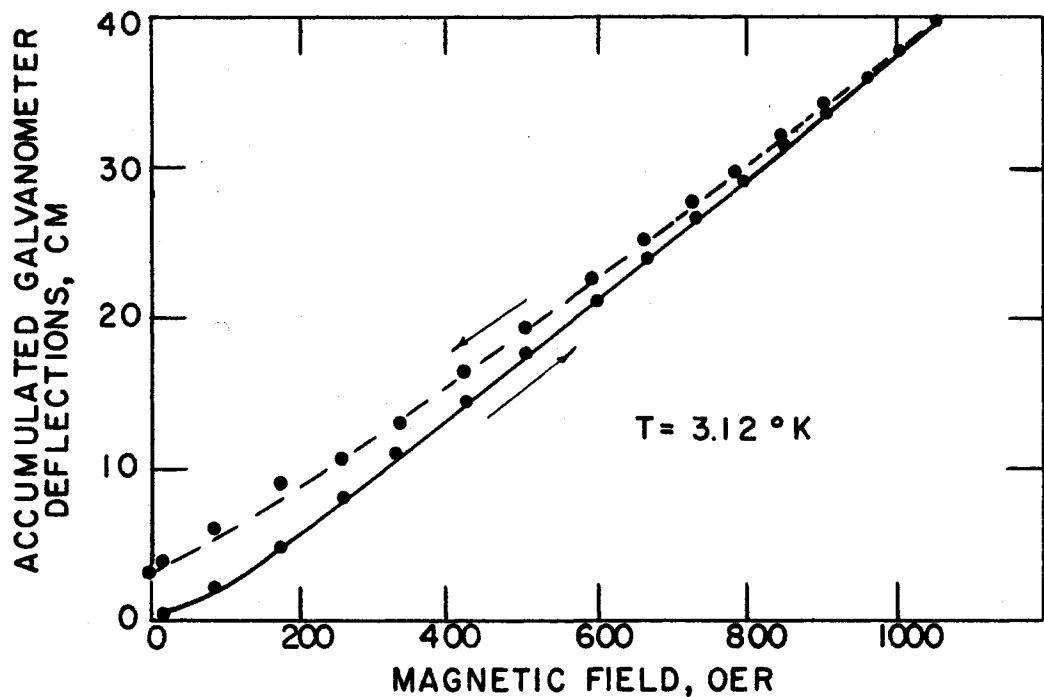


Figure 18. Accumulated galvanometer deflections as a function of longitudinal magnetic field for the alloy 80 per cent lanthanum and 20 per cent lutetium at 3.12°K . (The solid curve is for increasing field and the broken curve is for decreasing field.)

can be seen that this sample is strained to such an extent that it is now quite impossible to ascertain very definitely when field penetration begins. Figure 19 illustrates how the resistivity and the secondary voltage of the a.c. method vary with temperature in the presence of a magnetic field. Comparison with the plot of the secondary voltage as a function of temperature in the absence of any applied field, Figure 15, shows that this would indicate an initial slope of the critical field vs. temperature curve greater than 3,000 oer/deg, which certainly cannot be the equilibrium curve because of the values this would yield for the specific heat. Figure 20 shows an isotherm of the secondary voltage and the resistivity as a function of the applied field. This curve is consistent with the curves of Figure 19, which serve to illustrate that these methods are not useful for obtaining critical field data for substances of this nature.

Nature of the Substances

All samples examined in this investigation exhibited behaviors characteristic of alloys; irreversibility of the superconducting transition and a broad transition. This is the result of the samples being strained in some way, which is also evidenced by their high residual resistivity.

This irreversibility could be due to the structure of the samples. These substances prefer a close-packed

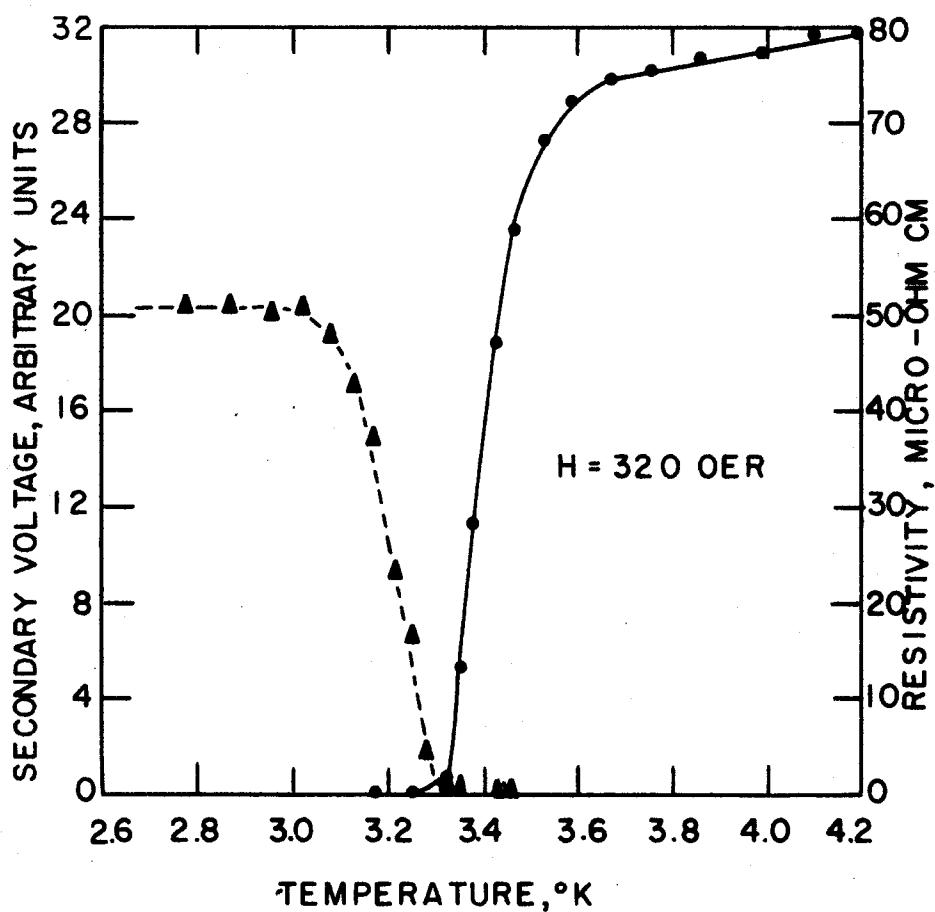


Figure 19. Secondary voltage and resistivity as a function of temperature for the alloy 80 per cent lanthanum and 20 per cent lutetium in a transverse magnetic field of 320 oer. (The solid curve is the resistivity and the broken curve is the secondary voltage.)

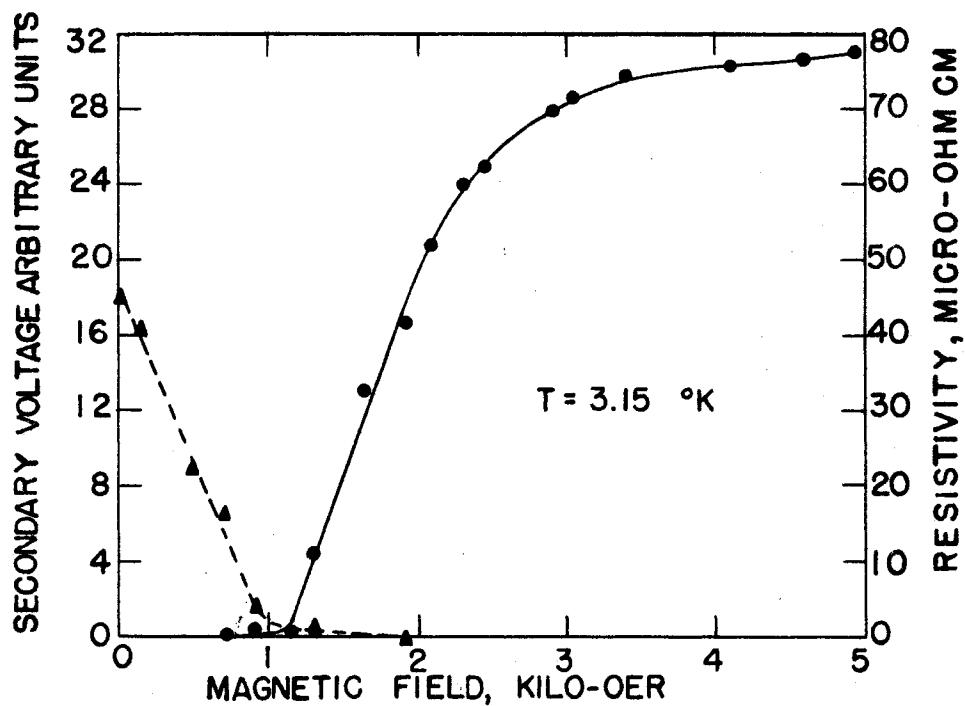


Figure 20. Secondary voltage and resistivity as a function of a transverse magnetic field for the alloy 80 per cent lanthanum and 20 per cent lutetium at the temperature of 3.15°K . (The solid curve is the resistivity and the broken curve is the secondary voltage.)

structure; however there seems to be a small energy difference between the various layer stacking sequences. This may mean that the layer stacking is not very regular, which would tend to broaden the transition since different structures have different transition temperatures.

Another possible cause for the irreversibility of the transition is impurity. Spectroscopic analysis indicates very little metal ion impurity; however hydrogen and oxygen, for example, may be present in relatively large amounts. Oxygen and nitrogen in interstitial positions in the vanadium lattice have been shown by Wexler and Corak (1952) to influence superconducting properties markedly. The presence of such impurities in the substances studied here is considered quite probable.

For the alloys studied there is the additional probability that there exists an inhomogeneity of concentration. This is a very common result when a solution of two liquid metals is cooled at a finite rate, according to Doan and Mahla (1941).

The irreversibility of the superconducting transition is very much in evidence in the d.c. work on face-centered cubic lanthanum. Here the longitudinal magnetic field was first increased and then decreased abruptly in steps. For each change of the magnetic field a flux change within the pick-up coil was observed. The broadness of the transition as observed in this manner was noted in a previous section.

In addition to this broadness the curve for decreasing magnetic fields is quite different from the curve for increasing magnetic fields. This difference is evidence for the fact that some flux becomes trapped by the substance. This is a consequence of the "spongy" structure as proposed by Mendelsohn (1935), which was discussed in an earlier section. The amount of flux trapped is quite high, being about 50 per cent. The percentage of flux trapped seems to increase for decreasing temperatures; however this aspect was not examined carefully. Also the percentage of flux trapped near the transition temperature, which has been considered by others such as Budnick, Lynton, and Serin (1956) and Pippard (1955), was not examined in any detail.

Factors Influencing Transition Temperatures

Crystal structure seems to play a very important role in superconductivity. In pure lanthanum the cubic form has a superconducting transition temperature nearly one degree higher than that for the hexagonal form. It seems to be a general rule that the superconducting transition temperatures are higher for cubic structures than for hexagonal structures, as noted by Matthias and Hulm (1952). For lanthanum the two observed structures seem to have the same volume per atom, so the structure would seem to be the only variable here. However there is presently no good explanation for the role of structure in superconductivity.

The atomic volume seems to play an important role in superconductivity. For the alloys of lanthanum with yttrium and lutetium the crystal structure and the number of conduction electrons per atom have been kept constant while the volume and mass have been varied. The lanthanum-yttrium series seemed to indicate that the superconducting transition temperature varied with volume to a much greater power than was found for the lanthanum-lutetium series. Matthias (1953) reported the transition temperature to be proportional to the volume to a power between four and ten, and inversely as the mass. It was not possible to determine the mass dependence of the transition temperature from this investigation.

The number of conduction electrons per atom was probably varied for only one alloy studied, the lanthanum-ytterbium alloy. The volume per atom for this alloy was very nearly the same as that for the hexagonal lanthanum which has the same structure. Hence it may be that this change is caused by the slight change in electron density; however since the lattice parameters were not determined precisely, it is not possible to rule out a difference in volume as being the cause of this shift.

SUMMARY

Superconductivity was observed in two crystal structures of pure lanthanum. The hexagonal close-packed form, which had the layer stacking sequence ABAC... instead of the usual ABAB..., had a transition temperature of 5.0°K. Face-centered cubic lanthanum had a transition temperature of 5.9°K.

Critical magnetic fields were determined for the face-centered cubic lanthanum, which was obtained in rather pure form. The initial slope of the critical magnetic field vs. temperature curve was found to be 550 oer/deg. This would correspond to a difference in specific heat of 0.103 cal/mole deg. for a reversible transition.

Alloys of lanthanum and yttrium were examined systematically. The same two crystal structures found in pure lanthanum were observed here. If we assume that the only variables affecting the transition temperatures for a particular structure are the volume and the mass we may obtain an expression for the transition temperature as a function of these for the hexagonal structure. The mass dependence could not be determined; however the transition temperature seemed to depend on the volume to a power a , where $a = 25 \pm 2$.

Alloys of lanthanum and lutetium were also examined. Again it was not possible to obtain the mass dependence,

however, the transition temperature seemed to depend on the volume to a power a , where $a = 9 \pm 2$.

The 95 per cent lanthanum and 5 per cent ytterbium alloy was the only one studied of these metals. Its transition temperature was 4.0°K .

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