

## Far-Infrared Absorption in Superconducting Lanthanum\*

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Measurements have been made of far-infrared absorption in pure, face-centered cubic, superconducting lanthanum at 1.3°K. The results indicate a gap width  $2\Delta = 12.0 \pm 1.0 \text{ cm}^{-1}$ . In terms of the measured value of the critical temperature,  $T_c = 6.06^\circ\text{K}$ ,  $2\Delta = 2.85 \pm 0.24 kT_c$ . The data indicate the possible presence of a small amount of structure in the absorption curve at an energy about twice the gap width. These results are compared with theoretical predictions which have been made recently from a proposed new mechanism for superconductivity in lanthanum.

### I. INTRODUCTION

THIS experiment was undertaken as the first step in a planned series to determine how the width of lanthanum's superconducting energy gap changes when small amounts of gadolinium are alloyed with the lanthanum. The observed sharp decrease in the critical temperature caused by dissolved gadolinium<sup>1</sup> is believed to result almost entirely from the exchange interaction between conduction electrons and the net spin of the core electrons of the gadolinium atoms.<sup>2-4</sup> One can guess from the observed critical temperatures that small amounts of gadolinium will sharply decrease the energy gap width in lanthanum. This is borne out by a theoretical calculation.<sup>4</sup>

Unfortunately, our measurements indicate that in pure lanthanum the gap width is somewhat less than we had expected. The far-infrared absorption edge falls so near the long-wavelength limit of our available wavelength range that it will not be possible to follow the expected decrease in gap width caused by dissolved gadolinium. Nevertheless, there has been a recent surge of interest in the superconducting properties of transition elements in general,<sup>5</sup> and of lanthanum in particular,<sup>6,7</sup> so we are reporting here the results of our experiment on pure lanthanum.

Because of the complex and difficult metallurgy of lanthanum, this work was performed as a joint project between the far-infrared group at Illinois and the group at Iowa State, which has had considerable experience in preparing and handling rare earths.

### II. SAMPLE PREPARATION

Lanthanum metal is known to exist in at least three allotropic modifications. The "as-cast" samples are apparently a mixture of the close-packed hexagonal (*abac*) and the face-centered cubic (*abc*) forms. In either of these forms, stacking faults readily occur, and even a single grain of the metal may exhibit a mixture of the properties of the hexagonal close-packed and the face-centered cubic modifications. In such samples the relative amounts of the two modifications will change with time, even at room temperature. In addition, lanthanum metal reacts very readily with the non-metallic elements such as oxygen, nitrogen, and hydrogen, so careful preparation and handling of the samples is required to avoid these impurities. Highly purified substances must be used in the production of lanthanum, since experience shows that most impurities in the starting materials end up in the reduced metal.

The lanthanum used in this investigation was prepared by calcium reduction of  $\text{LaF}_3$  in tantalum crucibles, as described by Spedding and Daane.<sup>8</sup> The calcium was freshly distilled, and was used in the form of large chunks (approximately 2 in.  $\times$  2 in.  $\times$  2 in.) to avoid the contamination usually encountered in grinding the calcium into small particles. The  $\text{LaF}_3$  was prepared in a platinum boat from high-purity  $\text{La}_2\text{O}_3$  (99.99+%) and highly purified  $\text{NH}_4\text{HF}_2$ . After the reduction, the slag was removed, and the lanthanum metal was placed in a tantalum crucible and heated by induction under vacuum to 1800°C to drive off the volatile impurities. The major impurities in the resulting metal are listed in Table I.

The lower limit for quantitative determination of impurities in lanthanum for the following elements in ppm

\* F. H. Spedding and A. H. Daane, *J. Metals* **6**, 504 (1954).

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<sup>1</sup> B. T. Matthias, H. Suhl, and E. Corenzwit, *Phys. Rev. Letters* **1**, 92 (1958).

<sup>2</sup> H. Suhl and B. T. Matthias, *Phys. Rev.* **114**, 977 (1959).

<sup>3</sup> W. Baltensperger, *Helv. Phys. Acta* **32**, 197 (1959).

<sup>4</sup> A. A. Abrikosov and L. P. Gor'kov, *Zh. Eksperim. i Teor. Fiz.* **39**, 1781 (1960) [English transl.: *Soviet Phys.—JETP* **12**, 1243 (1961)]. One can show from the equations in this article that at  $T=0^\circ\text{K}$ , the electromagnetic gap edge in the alloy should occur at an energy  $2\Delta_0 e^{-\nu} [1 - ((4/\pi) y e^{\nu})^{2/3}]^{3/2}$ , where  $2\Delta_0$  is the gap width in the pure metal at  $T=0^\circ\text{K}$  and  $y = (T_{c0} - T_c) / \Delta_0$ .  $T_{c0}$  is the critical temperature of the pure metal, and  $T_c$  is that of the alloy.

<sup>5</sup> J. W. Garland, Jr., *Phys. Rev. Letters* **11**, 111 (1963).

<sup>6</sup> D. C. Hamilton and M. A. Jensen, *Phys. Rev. Letters* **11**, 205 (1963).

<sup>7</sup> C. G. Kuper, M. A. Jensen, and D. C. Hamilton (to be published).

TABLE I. Analysis of lanthanum in ppm.

	O <sub>2</sub>	N <sub>2</sub>	F <sub>2</sub>	C	Fe	Ni
La	60±10	10±5	10±5	80±10	16±2	20±2

were: H<sub>2</sub>=5, Ca=500, Mg=200, Si=250, Cr=100, and Ta=500. Analyses were made for these impurities, and all were found to be below these limits. It was estimated from spectrographic analysis that the following elements were present in amounts less than indicated: H<sub>2</sub>=5 ppm; Ca=10 ppm; Mg=5 ppm; Si=60 ppm; and Cr=100 ppm. Ta was not detected spectrographically.

The sample consisted of four plates, each 4 in. ×  $\frac{13}{16}$  in. ×  $\frac{1}{16}$  in. thick. The plates were made separately by arc-melting 65 g of lanthanum on a water-cooled copper hearth into bars about  $\frac{1}{4}$  in. ×  $\frac{3}{4}$  in. ×  $3\frac{1}{4}$  in. Each bar was then rolled to a thickness of  $\frac{5}{32}$  in. and trimmed by shearing into plates  $\frac{7}{8}$  in. ×  $4\frac{1}{16}$  in. The plates were then milled to the desired sample size.

Since lanthanum combines readily with oxygen, nitrogen, and hydrogen, even at moderate temperatures, the final fabrication step was to file the surfaces of the plates smooth, just prior to placing them into separate tantalum envelopes, which previously had been outgassed. The envelopes were then to be welded shut. To prevent melting of the lanthanum during this operation, the envelopes were clamped between two large pieces of brass, with only the end to be welded protruding, and then quickly placed into the welder described by Miller *et al.*<sup>9</sup> The system was vacuum purged, and the envelope was welded shut under an atmosphere of helium. The tantalum envelopes containing the samples were heated for 16 h at 400°C in order to convert any hcp to fcc, and were then quenched by dropping them into water. Each envelope was leak-tested before and after the heat treatment. To prevent surface contamination, the samples were kept in the sealed tantalum envelopes until they were to be used.

To show that this procedure gave fcc lanthanum, trimmings were taken from the end and the side of a rolled specimen, and the surfaces were filed clean. The trimmings were then sealed in tantalum capsules, annealed at 400°C for 16 h, and quenched. The critical temperature of each trimming was measured by a 33

TABLE II. Critical temperature ( $T_c$ ) and transition width ( $\Delta T$ ) of annealed and quenched lanthanum.<sup>a</sup>

Position of trimming	$T_c$ (°K)	$\Delta T$ (°K)
End	6.05±0.02	0.02
Side	6.07±0.02	0.06

<sup>a</sup> Taken from a paper to be submitted for publication by D. K. Finne-more, F. H. Spedding, and B. J. Beaudry.

<sup>9</sup> A. E. Miller, A. H. Daane, C. E. Habermann, and B. J. Beaudry, *Rev. Sci. Instr.* **34**, 644 (1963).

cps mutual inductance method. Table II shows the measured values of the critical temperature and the transition widths. Ballistic measurements corroborated these results.

An x-ray diffraction pattern was taken at room temperature of the surface of a sample treated identically to that used for the far-infrared work. All of the observed diffraction peaks could be accounted for by a fcc cell with  $a=5.29$  Å, showing that the sample contained at least 95% fcc lanthanum.

The ratio between the resistivity at room temperature and that at 4°K has been found to be greater than 150. This is further evidence that no pronounced stacking faults were present in the fcc grains. While one does not have techniques for etching pure lanthanum to give good metallographic pictures showing grain boundaries, metallographic studies were made on these samples using techniques which have been successful in showing second-phase impurities in yttrium and impure lanthanum. No evidence of any such impurities were observed. This provides an indication of the high purity of this material.

### III. FAR-INFRARED MEASUREMENTS

The four plates of lanthanum, fabricated in the manner described above, were taken from their tantalum capsules and put in a holder, in which they formed a pyramidal cavity with a shape and size similar to the conical cavity used in previous far-infrared investigations.<sup>10</sup> During this process, the sample was exposed to air for 45 min.

We have described elsewhere<sup>10</sup> the method by which the far-infrared measurements were made, so a brief description here will suffice. The sample was held at a temperature of 1.3°K during the measurements. The radiation was brought into the cavity through a small hole. A bolometer in the cavity measured the energy density. Since the radiation beam was chopped, an ac signal was generated by the bolometer, and the signal was measured with a lock-in amplifier. By dividing the bolometer signal  $P_S$  when the cavity was superconducting by the signal  $P_N$  when the cavity was forced into the normal state by a magnetic field of 3800 Oe, one obtains the ratio  $P_S/P_N$  for a given far-infrared wavelength. As the wavelength is decreased, this ratio decreases when the superconducting metal begins to absorb radiation. This onset of absorption indicates the gap edge. It has been shown<sup>11</sup> that  $(P_S/P_N) - 1$  is approximately proportional to  $R_N - R_S$ , where  $R_N$  and  $R_S$  are the surface resistances of the cavity walls in the normal and superconducting state, respectively. In a given run, all data for the superconducting cavity were obtained before those for the normal cavity. This avoided complications which might have seen generated by trapped

<sup>10</sup> J. D. Leslie and D. M. Ginsberg, *Phys. Rev.* **133**, A362 (1964).

<sup>11</sup> P. L. Richards and M. Tinkham, *Phys. Rev.* **119**, 575 (1960).

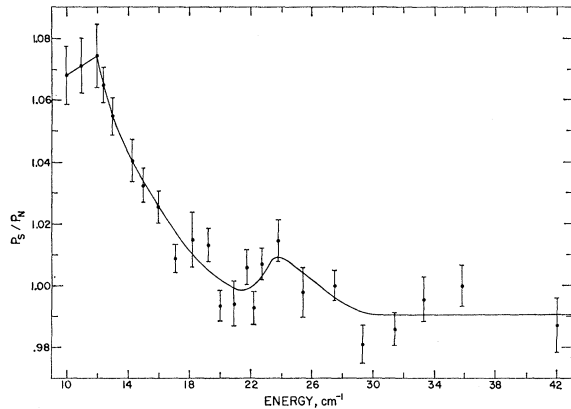


FIG. 1. Far-infrared absorption curve of fcc lanthanum.  $P_S$  and  $P_N$  are defined in Sec. III of the text. The error bars indicate plus and minus one standard deviation.

magnetic flux. The sensitivity of the equipment was monitored by a reference cavity signal so that one could correct for slow drifts. Measurements of  $P_S$  and  $P_N$  were made many times at each wavelength, to average over noise. The absorption curve determined in this way is shown in Fig. 1. The error bars indicate plus and minus one standard deviation, as determined from a statistical analysis of the data for each wavelength.

#### IV. DISCUSSION

The absorption curve in Fig. 1 indicates that the main gap edge in superconducting lanthanum is at  $12.0 \pm 1.0 \text{ cm}^{-1}$ . Using a value  $6.06^\circ\text{K}$  for the critical temperature of lanthanum (the average of the two values in Table II), this yields a value  $2.85 \pm 0.24 kT_c$  for the gap width, sometimes denoted by  $2\Delta$  or  $2\epsilon_0$ . This is somewhat lower than predicted by BCS<sup>12</sup> ( $3.5 kT_c$ ), and is also lower than observed for most superconductors ( $3.2 kT_c$  to  $3.8 kT_c$ ).<sup>13</sup> At the present time, we are unable to account theoretically for the unexpectedly low ratio of gap width to  $kT_c$  in lanthanum, but it seems well worth further experimental and theoretical investigation.

<sup>12</sup> J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

<sup>13</sup> D. H. Douglass and L. M. Falicov, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, to be published), Vol. IV.

The small structure which is indicated by Fig. 1 at an energy about twice the gap width is not unlike that observed by Richards above the main gap edge in the far-infrared absorption curve of superconducting tin.<sup>14</sup> Our data are not precise enough to show the shape of the structure, or even to be sure beyond all doubt that it is real, so it might seem premature to speculate about its origin. However, one possible explanation for it is given below.

It is interesting to compare our value for the gap width to that predicted recently by a theory of Kuper, Jensen, and Hamilton,<sup>6,7</sup> which came to our attention after our far-infrared measurements were completed. They speculate that there is a narrow  $f$  band slightly above the Fermi surface in lanthanum. They show that this band should be partially occupied in the ground state of the superconductor, because of an antiferromagnetic exchange interaction between the electrons in this band. They predict that there are two gap widths, one for the conduction electrons,  $2\Delta_s \lesssim 2kT_c$ , and one for the  $f$  electrons,  $2\Delta_f \gtrsim 10kT_c$ . Our experimental value for  $2\Delta$  is not in disagreement with their value for  $2\Delta_s$ , within the accuracy of their calculation. If there is a larger gap at around  $10 kT_c$  ( $42 \text{ cm}^{-1}$ ), then the electrons associated with that gap must absorb very little energy at our infrared frequencies. This conclusion rests on the close approach of our absorption curve to unity for photon energies greater than about  $30 \text{ cm}^{-1}$ .<sup>15</sup> It is, of course, possible that our small structure at about  $24 \text{ cm}^{-1}$  indicates the predicted second gap edge, which would then be at a lower energy than calculated.

#### ACKNOWLEDGMENTS

We thank Professor J. Bardeen and Professor L. P. Kadanoff for interesting discussions of the effect of magnetic impurities on the properties of superconductors. We also thank Dr. C. G. Kuper *et al.* for giving us a preprint of their theory.

<sup>14</sup> P. L. Richards, Phys. Rev. Letters **7**, 412 (1961).

<sup>15</sup> Although second-order effects coming from a small dependence of our bolometer sensitivity on magnetic field destroy the significance of the precise *absolute* values of  $P_S/P_N$ , one can compare the curve of Fig. 1 with curves for other superconductors measured with the same bolometer and similar bolometers. This comparison indicates that the absorption curve of lanthanum has a value within one percent of that of other superconductors at frequencies larger than  $2\frac{1}{2}$  times the gap width.