

# Effect of Pressure on the Superconducting Transition Temperature of Lanthanum\*

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The variation of the superconducting transition temperature of hcp lanthanum has been measured as a function of pressure up to 10 kbar. An approximately linear increase of  $T_c$  with applied pressure was observed ( $\partial T_c / \partial P \sim 14 \times 10^{-5} \text{ }^\circ\text{K bar}^{-1}$ ). The relation of this behavior to two recently proposed theories for the superconductivity of lanthanum is discussed.

## I. INTRODUCTION

IN view of the recent suggestions by Kondo<sup>1</sup> and Kuper, Jensen, and Hamilton<sup>2</sup> for the mechanism responsible for the occurrence of superconductivity in lanthanum it was decided to study the effect of pressure upon the superconducting transition temperature. Both mechanisms evoke either a narrow band or a sharp 4f level lying just above the Fermi surface. Kondo proposed that there is an interaction between this narrow band, irrespective of whether it is empty or partially occupied, and the conduction band.<sup>3</sup> He then showed, using the BCS formalism for the electrons in the conduction band, that the presence of this narrow band increased the superconducting transition temperature. Kuper *et al.*, on the other hand, suggested that it is a magnetic interaction, arising from the partial occupation of the nearby 4f level, which gives rise to the necessary electron-electron interaction for superconductivity in lanthanum. In both theories the value of the superconducting transition temperature  $T_c$  is dependent on the magnitude of the energy gap between the 4f band and the Fermi surface, and both theories predict that as the energy gap increases  $T_c$  will decrease.

It is known that the application of a sufficiently high pressure ( $\sim 8$  kbar) at room temperature to the normal face-centered cubic ( $\gamma$ ) phase of cerium results in a collapse to a denser ( $\alpha$ ) phase,<sup>4</sup> but without a change of structure.<sup>5</sup> It has been suggested<sup>6,7</sup> that this transition is associated with the transfer of the single localized 4f electron in  $\gamma$  cerium into the conduction band of  $\alpha$  cerium. Evidence in agreement with this suggestion has been obtained from low-temperature paramagnetic scattering of neutrons from cerium by Wilkinson, Child, McHargue, Koehler, and Wollan<sup>8</sup> who were able to

interpret their data assuming zero localized moment in  $\alpha$  cerium. It may be argued, therefore, that the application of pressure to cerium results in a displacement of the 4f level to a higher energy relative to the Fermi surface. Allowing that the application of pressure tends to raise the 4f level in cerium, it may also be argued that this will be true for the unoccupied 4f level in lanthanum. As a consequence of such a movement of the 4f level on the application of pressure and on the basis of the above theories, one would expect a dramatic decrease in the superconducting transition temperature of lanthanum.

It has been observed that the majority of superconductors show an increase in volume below the superconducting transition temperature. A simple thermodynamic argument leads one to expect that  $T_c$  will decrease upon the application of pressure which is in agreement with observation. Lanthanum, however, is anomalous and shows a *decrease* in volume<sup>9</sup> below the superconducting transition temperature. Therefore one would expect  $T_c$  to increase with pressure, in contradiction to the prediction of the above theories.

The purpose of the following is to attempt to clarify the position by a report of some preliminary measurements of the variation of the superconducting transition temperature of lanthanum under pressure.

## II. MEASUREMENTS

Measurements were made on samples of lanthanum obtained from two separate sources. One sample was kindly supplied by the U. S. Bureau of Mines, denoted as U.S.B.M., and the other was obtained from the Lunex Company. The analyses in wt%, as supplied with the samples, gave the following impurities: U.S.B.M. O 0.016, C 0.047, Al 0.01, Fe 0.006, Mo 0.014, Si 0.012, Ce 0.07; Lunex O 0.08, Fe 0.01, Mg 0.01, Nb 0.015, Nd 0.01, Er 0.01, all other impurities were less than 0.01 wt% in both cases.

Pressure applied to the sample, in a pressure capsule, at room temperature was retained by a clamp technique (Bowen and Jones<sup>10</sup>). The sample was cooled to its superconducting transition temperature by suspension over a bath of liquid helium. Temperatures were measured with a calibrated carbon resistor mounted

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<sup>1</sup> J. Kondo, Progr. Theoret. Phys. (Kyoto) **29**, 1 (1963).

<sup>2</sup> C. G. Kuper, M. A. Jensen, and D. C. Hamilton, Phys. Rev. **134**, A15 (1964).

<sup>3</sup> Kondo labeled this as an *s* band for convenience, but we shall assume that it is an admixture of *s*, *p*, *d*, and *f* wave functions in the particular case of lanthanum.

<sup>4</sup> P. W. Bridgman, *The Physics of High Pressures*, (G. Bell and Sons, London, 1952).

<sup>5</sup> A. W. Lawson and T. Tang, Phys. Rev. **76**, 301 (1949).

<sup>6</sup> L. Pauling, quoted in J. Chem. Phys. **18**, 145 (1950).

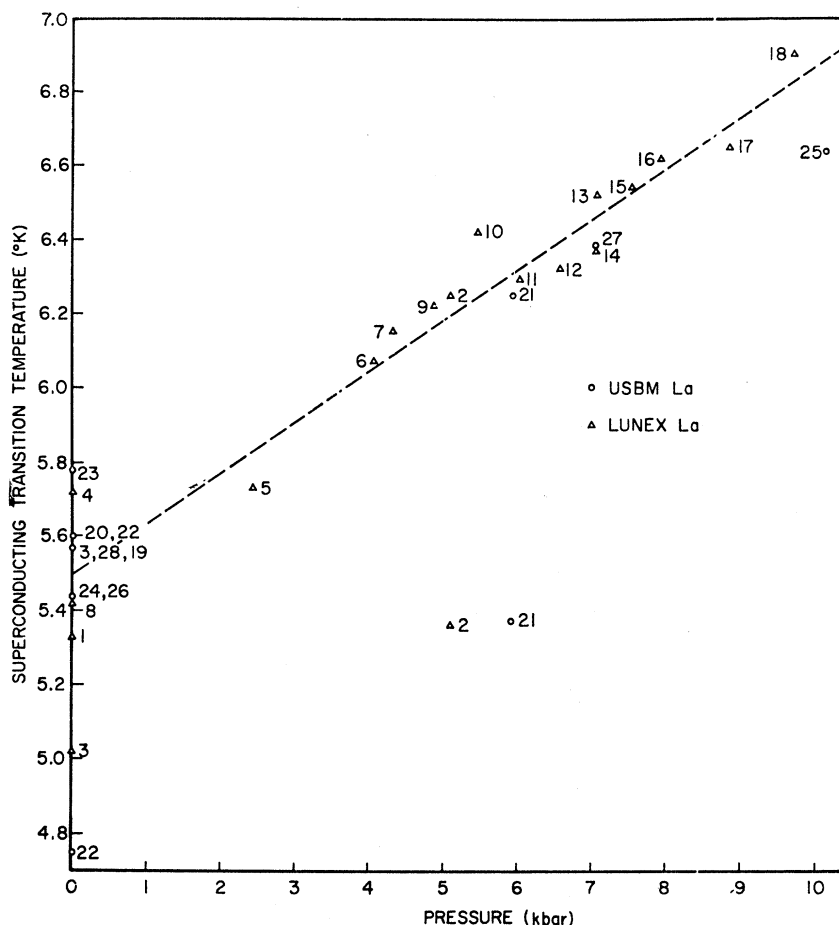
<sup>7</sup> W. H. Zachariasen, quoted in Acta, Met. **8**, 637 (1960).

<sup>8</sup> M. K. Wilkinson, H. R. Child, C. J. McHargue, W. C. Koehler, and E. O. Wollan, Phys. Rev. **122**, 1409 (1961).

<sup>9</sup> H. Rohrer, Helv. Phys. Acta **33**, 675 (1960).

<sup>10</sup> D. H. Bowen and G. O. Jones, Proc. Roy. Soc. (London) **A254**, 522 (1960).

FIG. 1. The variation of the superconducting transition temperature of lanthanum with applied pressure.



in the base of the pressure capsule. The superconducting transition was detected by a standard ac bridge technique, with a signal frequency of 1 kc. The amplified and rectified off-balance signal, due to the onset of superconductivity, was used to drive the  $Y$  axis of a Moseley Autograf  $X$ - $Y$  recorder. The potential drop across the carbon resistor was used to drive the  $X$  axis. In this manner superconducting transitions could be continuously recorded.

The "as received" U.S.B.M. and Lunex samples were subjected to mechanical and thermal treatment respectively to render as much as possible of the sample into the hcp phase.<sup>11</sup> Before the initial  $T_c$  of the U.S.B.M. sample was measured, it was strained by the brief application of a pressure equal to the maximum used. The Lunex sample was sealed in an evacuated quartz tube, annealed at 250°C for 25 h, and quenched in water. Following these treatments both samples had transition temperatures of about 5.5°K which is higher than the accepted value for the hcp phase of lanthanum as determined by resistive<sup>12</sup> and calori-

metric<sup>13,14</sup> measurements. However, the transition temperature, as determined by induction measurements<sup>15,16</sup> is in slightly better agreement. It was also observed that all subsequent atmospheric-pressure transitions were distributed about 5.5°K.

The majority of the superconducting transitions measured were relatively sharp for a "hard" superconductor, even at the highest pressures used in this investigation. At least 90% of the atmospheric pressure transitions took place over a temperature interval of 0.1–0.2°K, the transitions at high pressure being about 0.2°K wider. If we attributed the entire increase in transition with to a departure from hydrostatic pressure conditions, this would correspond to a pressure inhomogeneity of 10–20%.

Transition temperatures for a number of pressures up to 10 kbar are plotted in Fig. 1. The sequence of the measurements is indicated by the number beside

<sup>13</sup> A. Berman, M. W. Zemansky, and H. A. Boorse, *Phys. Rev.* **109**, 70 (1958).

<sup>14</sup> D. K. Finnemore, D. L. Johnson, J. E. Ostenson, F. H. Spedding, and B. J. Beaudry (to be published).

<sup>15</sup> G. S. Anderson, S. Legvold, and F. H. Spedding, *Phys. Rev.* **109**, 243 (1958).

<sup>16</sup> J. Müller and M. Risi, *Helv. Phys. Acta* **33**, 459 (1960).

<sup>11</sup> W. T. Ziegler, R. A. Young, and A. L. Floyd, Jr., *J. Am. Chem. Soc.* **75**, 1215 (1953).

<sup>12</sup> K. Schwidtal, *Z. Physik* **169** 564 (1962).

each point. Transition temperature rather than change in transition temperature is plotted due to the lack of reproducibility of the atmospheric pressure  $T_c$  after releasing the applied pressure. It is concluded that the  $T_c$  for lanthanum is sensitive to internal strains, and this is reflected in the variation of  $T_c$  on removal of the applied pressure. Despite this variation in the values of  $T_c$  at atmospheric pressure there is a roughly linear dependence of the transition temperature with applied pressure. ( $\partial T_c / \partial P \sim 14 \times 10^{-5}$  °K/bar).

Measurements 2 and 21 are of special interest as two distinct transitions, approximately 1°K apart, were observed at pressures of 5150 and 5980 bar, respectively. On removal of the pressure the two transitions remained, but were displaced to lower temperatures (points 3 and 22). This behavior was observed in both samples examined, points 2 and 3 being for the Lunex sample and 21 and 22 for the U.S.B.M. Annealing at 250°C for several hours removed the double transition at atmospheric pressure in both cases (points 4 and 23). This behavior was not repeated in a subsequent measurement (point 10) on the Lunex sample in this pressure range. It should be noted that no anomalies in the compressibility<sup>17</sup> and the electrical resistance<sup>18</sup> have been reported in this pressure range.

### III. DISCUSSION

Thus the observed increase of  $T_c$  with applied pressure precludes the models of Kondo and Kuper *et al.* for the superconducting mechanism in lanthanum, if the premise that the application of pressure raises the  $4f$  level relative to the Fermi surface is accepted. This observed increase is, however, in qualitative agreement with the observed volume change and a direct application of the Clausius-Clapeyron relation. Using data obtained on the critical field behavior of lanthanum, his measured volume change and the compressibility, Rohrer<sup>9</sup> estimated a value of  $d \ln T_c / d \ln V \sim -0.5$ . From the observed  $d T_c / d P$  in the present work and the room temperature compressibility of lanthanum we estimate a value of  $d \ln T_c / d \ln V \sim -6$ , which is an order of magnitude greater than that given by Rohrer. This

discrepancy is perhaps not surprising in view of the irreversible magnetic behavior of lanthanum.<sup>14</sup>

If we adopt a BCS approach to the superconducting behavior of lanthanum then the maximum increase in  $T_c$  under pressure may be accounted for by an increase of 8% in the density of states, if we assume the electron-phonon interaction is constant. Such an increase is quite feasible if the Fermi energy of lanthanum occurs near a peak in the density-of-states curve and this is not unreasonable since lanthanum is an element with a high density of states.<sup>13</sup> However, a high density of states alone is not sufficient to account for the superconducting behavior of lanthanum since scandium, yttrium and lutetium have roughly the same value for their densities of states<sup>19</sup> and are not superconducting above 0.1°K. We think, therefore, that the amount of  $f$  admixture in the wave functions at the Fermi energy must be an important feature in the superconductivity of lanthanum.

Finally it may be argued that part of the increase in  $T_c$  is associated with the transition of the hcp phase to the fcc under pressure. However, we think such an explanation is unlikely since the transformation pressure at room temperature for hcp to fcc is believed to be  $\sim 23$  kbars.<sup>17,20-23</sup> Some unsuccessful attempts have been made to obtain the fcc phase of lanthanum by quenching from 600°C. We were, however, unable to obtain a sample with a sharp superconducting transition around 6.0°K. This may be because the sample size ( $\frac{3}{8}$ -in.-diam.  $\frac{3}{8}$ -in.-long cylinders) was too great and hindered the fast quench necessary to retain the fcc phase.

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<sup>23</sup> D. B. McWhan and W. L. Bond, Rev. Sci. Instr. **35**, 626 (1964).

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<sup>18</sup> P. W. Bridgman, Am. Acad. Arts. Sci. **79**, 149 (1951).