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Superconducting Transition Temperature of La_3S_4

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The superconducting transition temperature of stoichiometric La_3S_4 has been measured by two different methods and has been found to be (8.25 ± 0.2)°K. A range of superconducting compositions exists in the metal-rich end of the γ phase of lanthanum sulfide. Part of the sulfur-rich end of the γ phase is nonsuperconducting. The superconducting transition temperature of γ-phase lanthanum sulfide appears to increase with increasing lanthanum content.

THE compound La_3S_4 has recently been reported[1] to be a superconductor with a transition temperature of 6.5°K. Experiments conducted in this laboratory have shown that the Th_3P_4 phase of the lanthanum-sulfur system contains a range of superconducting compositions. However, these experiments have shown that the transition temperature for La_3S_4 is 8.25 ± 0.2°K, rather than 6.5°K.

The lanthanum-sulfur system crystallizes in a defect lattice of the Th_3P_4 type[2] over the composition range $La_{12-x}G_xS_{16}$, where $0\leq x\leq\frac{4}{3}$, and where G represents an unoccupied lanthanum side in the lattice. This region of the lanthanum-sulfur phase diagram is called the γ phase.

We have found that the superconducting transition temperatures of the γ-phase lanthanum sulfides is a function of composition, with higher transition temperatures being associated with higher lanthanum content. A similar behavior was reported by Bozorth *et al.*,[1] for the lanthanum selenides.

The dependence of T_c on composition may be used to explain the apparent discrepancy between the results for La_3S_4 in the two laboratories if it is assumed that the lanthanum sulfide sample of Bozorth *et al.*, was actually more sulfur-rich than was reported. The possible difference in composition between the sample of Bozorth *et al.*, and sample materials of nominal La_3S_4 composition in the present work may be due to the use of two different methods of preparation of sample material in the separate laboratories. The samples of this report were made with La_2O_3 as a starting material. This was sulfurized by an H_2S gas stream at 1400°C in a graphite reaction vessel,[3] and the resulting LaS_3 was zone refined in a vacuum at temperatures in excess of 2000°C. The particular operating temperature used in the zone refining procedure depended upon the composition sought, and was an increasing function of the desired final lanthanum content. Castings containing significant regions of La_3S_4 composition were produced by operation at temperatures high enough to result in mixed-phase regions of LaS-La_3S_4 in the early freezing part of the zone-refined material. These temperatures were in the range of 2200 to 2700°C. Samples of nominal La_3S_4 composition were cut from those parts of the cast zone-refined ingot which were immediately adjacent to regions exhibiting LaS inclusions in the La_3S_4 matrix. The samples were inspected to insure that no LaS was evident in the chosen piece. Density measurements indicate that such a procedure yields samples of low vacancy concentration, and such a conclusion is in agreement with phase diagram studies of other lanthanum chalcogenides.[4]

The sample with the lowest electrical resistivity of those shown in Fig. 1 was prepared by this method, and has an indicated electron concentration of 6.3×10^{21} electrons/cm^3, based on room-temperature measurements of the Hall coefficient. The electron concentration[5] thus measured has been found to be an increasing function of lanthanum content. Therefore, from the carrier concentrations indicated in Fig. 1 we see that the samples having the higher electrical resistivities have the lower lanthanum contents.

Complete superconductivity has been detected by the four-probe method at temperatures as high as 8.05°K. The highest temperature at which initial indications of superconductivity have appeared is 8.25°K. Thus the transition region has been found to be as narrow as 0.2°K. The sample of lowest resistivity in Fig. 1 exhibits a transition region of this narrow type and is believed to be essentially stoichiometric.

The LaS_x sample of intermediate resistivity in Fig. 1 shows an inclination towards superconductivity at temperatures below 8.25°K, but the transition does not become complete in the temperature range covered ($T>1.4$°K) and it is not abrupt. This observed be-

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[1] R. M. Bozorth, F. Holtzberg, and S. Methfessel, Phys. Rev. Letters **14**, 952 (1965).

[2] W. H. Zachariasen, Acta Cryst. **2**, 57 (1949).

[3] E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Giles, and N. F. Longren, J. Am. Chem. Soc. **72**, 2250 (1950).

[4] J. F. Miller, L. K. Matson, and R. C. Himes, *Rare Earth Research II*, edited by K. S. Vorres (Gordon and Breach Science Publishers, Inc., New York, 1964), p. 135.

[5] The designated electron concentrations of Fig. 1 are based on the assumption that $n=R^{-1}e^{-1}C^{-1}$ where R is the room-temperature Hall coefficient. The known valences of lanthanum and sulfur, would indicate that the actual electron concentration should be given by

$$n=(4-3X)/a^3,$$

where a is the lattice constant and has the value 8.73 Å. This formula yields the value 5.95×10^{21}/cm^3 for n, for the composition La_3S_4. This value is in rough agreement with the result obtained experimentally from the measurement of the Hall coefficient.

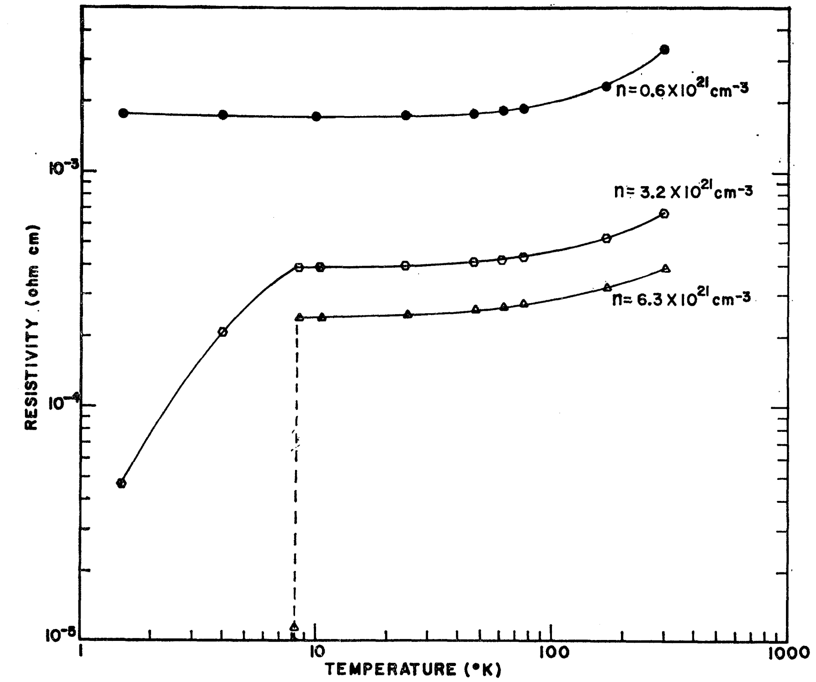

FIG. 1. Resistivity versus temperature for three separate four-probe resistivity samples of γ-phase lanthanum sulfide. Indicated electron concentrations are based on Hall-effect measurements. The sample of lowest resistivity is nominally La_3S_4. The superconducting transition region for this sample extends between 8.25°K and 8.05°K with an error of a few hundredths of one degree at each end of the range.

havior is probably due to inhomogeneities which cause the various microscopic regions of the sample to become superconducting at temperatures which depend upon the local composition.

Samples have been observed in which the final disappearance of resistance occurred at a temperature which was strongly dependent on the placement of the voltage probes. This behavior is also interpreted as being due to the inhomogeneity of the sample and the dependence of transition temperature on composition.

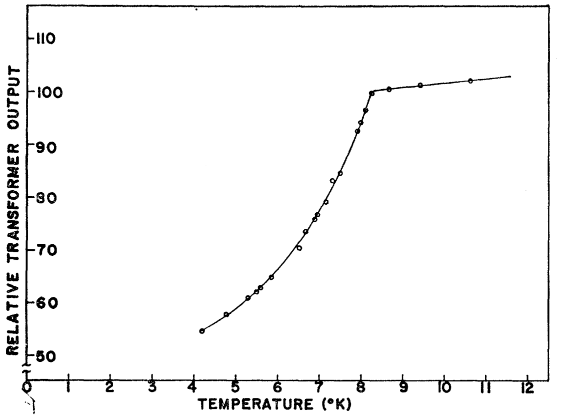

FIG. 2. Output voltage versus temperature for a constant-current 270-cps input of a transformer having a γ-phase lanthanum-sulfide core. The core material was finely powdered and was obtained from the lanthanum-rich end of a cast ingot which contained LaS inclusions.

The most sulfur-rich sample of Fig. 1 shows a negative value for $d\sigma/dT$ at temperatures below 10°K, being slightly suggestive of semiconductor behavior. Apparently superconductivity does not extend throughout the γ phase. This is not surprising as La_2S_3 is known to be an insulator.

To insure that the observed value of T_c for stoichiometric material was not due to a filamentary impurity, such as La_3Se_4, we have conducted tests on a pulverized sample which contained significant amounts of material of La_3S_4 composition. This powdered sample was used as the core of a transformed at 270 cps. The mutual inductance of the transformer was observed as a function of temperature. The results of this experiment are shown in Fig. 2. The La_3S_4 transition temperature obtained from the knee of the graph is (8.25 ± 0.1)°K, which agrees with that obtained from the four-probe resistivity measurements. Calibration of the transformer by means of a Pb granule core of identical geometry showed that the γ-phase lanthanum sulfide powder was approximately 100% superconducting at the lowest temperatures of the graph of Fig. 2. Similar tests on LaS gave results that could best be explained by assuming that the LaS under test was nonsuperconducting but contained a small percentage of La_3S_4 as a contaminant.

ACKNOWLEDGMENT

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