Å for Al, it is reasonable that the highly disordered films used in these experiments might not exhibit surface superconductivity. It should, however, be possible to perform further experiments of this type in which the ratio of d_G to l is small enough to give rise to surface coherence of the type predicted by Ginzburg and Kirzhnits.

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SUPERCONDUCTING LANTHANUM CHALCOGENIDES

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The compounds La_3Se_4 and La_3S_4 have been found to be superconducting below 8.6°K and 6.5°K, respectively. These materials crystallize with the bcc Th_3P_4-type structure which extends in a solid-solution system to the 2:3 compound.[1] The electrical properties vary with decreasing La concentration from metallic to semiconducting without measurable variation of lattice constant. In the analogous Gd system, ferromagnetism has been observed as a consequence of indirect exchange via conduction electrons.[2] Since the Gd and La compounds form solid solutions, it is possible to study the effect of magnetism on superconductivity as a function of Gd concentration.

The lanthanum chalcogenides are prepared by vapor reaction in evacuated quartz tubes at 600°C, and then sintered in sealed Mo containers to dense polycrystalline ingots. Micrometallurgical investigation shows single-phase materials with grains of 0.1- to 1.0-mm size. X-ray diffractometer analysis on single crystals indicates that the most probable space group is $I\bar{4}3d$-T_d^6, with $a_0 = 9.05$ and 8.73 Å for La_3Se_4 and La_3S_4, respectively. The semiconducting 2:3 compounds have the same lattice constants as the metallic 3:4 compounds and a high concentration of disordered defect sites in the cation lattice, which become completely filled at the 3:4 composition. Details of the structure will be discussed elsewhere.[3]

The superconductivity was detected by the observation of magnetic moments measured with a pendulum magnetometer[4] in fields of 0.1 to 25 kOe at 1.25°K and above.[5] The samples had irregular shapes, approximating spheres.

Figure 1 shows the hysteresis loops measured on La_3S_4 and La_3Se_4 at 1.3 and 1.25°K, respectively. It is apparent that these materials are type-II superconductors with the first critical field $H_{c1} \approx 0.15$ kOe for La_3S_4 and 0.2 kOe for La_3Se_4; the upper critical field H_{c2} is above the range of magnetic field strengths available in the equipment used. The jump between the upper and lower branches of the hysteresis loop is obtained by increasing the applied field from 20 to 21 kOe and reducing again to 20 kOe. Change in magnetization of

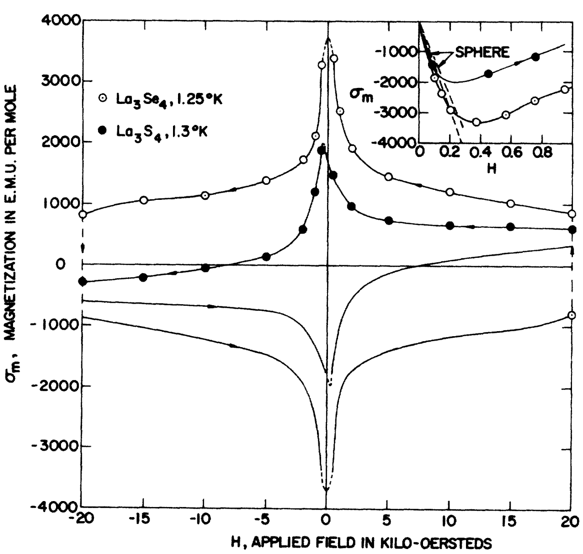

FIG. 1. Hysteresis loop and initial magnetization curves of La_3S_4 and La_3Se_4 showing superconductivity.

this type can be compared with the minor loops below H_{c2} observed in other type-II superconductors.[5]

The slight paramagnetism in La_3S_4, indicated in Fig. 1 by the difference in the positive and negative ordinates at the maximum field, may be due to paramagnetic impurities.

The inserts in Fig. 1 give experimental data on the initial magnetization. There is reasonable agreement with the initial slope calculated for a superconducting sphere, as expected for a homogeneously superconducting sample.

The critical temperatures T_c were derived from the temperature dependence of frozen-in magnetic flux. After the field $H = +20$ kOe had been applied, the moment was measured in a field of $H = -0.5$ kOe. The moments σ_m thus obtained for La_3Se_4 and La_3S_4 correspond to the near-peak values of the hysteresis loops in Fig. 1 and are plotted as functions of temperature in Fig. 2. Since the transition to the normal state can be characterized by the disappearance of frozen-in flux, the extrapolation of the measured moments to zero can be used to determine the value of T_c in an applied field of -0.5 kOe. The extrapolation yields $T_c = 6.5$°K for La_3S_4, and 8.6°K for La_3Se_4, with a probable error of a few tenths of a degree.

As the composition is changed in the solid-solution range from 3:4 to 2:3, the transition temperature is found to decrease rapidly toward zero. When the concentration deviates from 3:4 towards 1:1, the excess La forms LaSe as a second phase as identified by x-ray and micrometallurgical analysis. Therefore, our results are consistent with the phase equilibrium diagram, which excludes the existence of free La metal as a superconducting impurity in La_3Se_4. Measurement of the 2:3 and 1:1 compounds show only slight diamagnetic effects that can be accounted for by the presence of

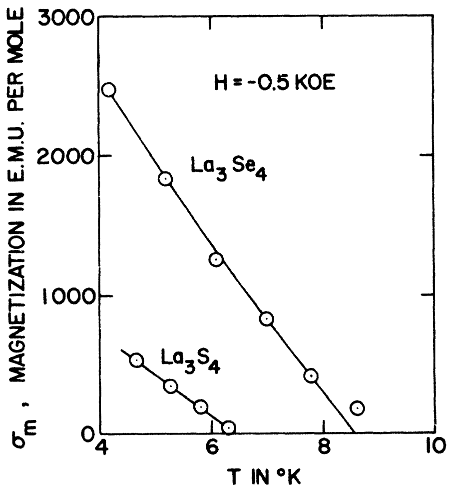

FIG. 2. Determination of critical temperature for superconductivity by measurement of σ_m in weak negative field after application of strong positive field, at near maximum of frozen-in flux. $T_c = 6.5$°K for La_3S_4 and 8.6°K for La_3Se_4.

small amounts of 3:4 impurities, and are therefore considered to be nonsuperconducting.

Our present results open the way to further studies of the influence of the conduction-electron concentration, lattice spacing, and defects on superconductivity and its relation to ferromagnetism.

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