LATTICE INSTABILITY (BCC-TETRAGONAL TRANSITION) AND SUPERCONDUCTIVITY IN "La_3X_4" BASE MATERIALS (X = S OR Se)

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The effect of substitution of Ca, Y, Ce and Th for La in LaS_x on T_c and T_M (bcc - tetragonal transformation temperature) was studied. In both the LaS_x and $LaSe_x$ systems T_M increases as the sulfur to metal ratio approaches 1.333 (La_3X_4). T_c increases in both the tetragonal and bcc phases as the sulfur to metal ratio approaches the concentration at which T_M = 0 K. Low temperature heat capacity measurements in fields up to 10 T show that both LaS_x and $LaSe_x$ are high magnetic field superconductors ($H_{c2}(0)$ ~ 15 T). The pressure variation of T_c for four LaS_x (x = 1.346 to 1.433) samples was determined up to 20 kbar.

I. INTRODUCTION

Recently Ikeda et al. (1980 and 1982) have shown that the superconducting properties of the stable cubic form of "La_3S_4" are optimum for the composition at which the bcc-tetragonal transformation temperature (T_M) is 0 K (the critical composition, x_c, is 1.362 for LaS_x). In the composition region where the bcc structure is stable down to 0 K ($1.362 \leq x \leq 1.500$), the superconducting transition temperature (T_c) and the upper critical field at 0 K [$H_{c2}(0)$] increase with decreasing x. For $x < x_c$ the tetragonal phase becomes the stable phase, and as x decreases to 1.333 (La_3S_4) T_M increases, T_c appears to remain constant and $H_{c2}(0)$ decreases. A comparison of the extrapolated T_c and $H_{c2}(0)$ values for the hypothetical cubic La_3S_4 (11 K and 14 T, respectively) with the corresponding observed values for the stable tetragonal La_3S_4 phase (8.2 K and 6 T, respectively), suggests that if the bcc to tetragonal transformation could be prevented, the superconducting properties of LaS_x would be improved.

In addition to the influence of lattice instabilities on the superconducting properties of LaS_x, the increase in T_c with pressure of "La_3S_4" is one of the largest known. Previous work which showed a monotonic increase in T_c and an increase in slope (dT_c/dp) with pressure to 21 kbar (Shelton et al. 1975), has been extended to 45 kbar indicating a maximum in T_c of 12.5 K at 22 kbar (Eiling, et al., 1981). Furthermore, elastic constant measurements on "La_3S_4" (Ford, et al. 1980) have indicated that the large pressure dependence of T_c remains anomalously large even when considered in terms of the physically more meaningful parameter of volume.

Because of these unusual properties our studies were extended to determine: (1) the effect alloying on T_M and T_c of LaS_x by substitution of various metals for La, (2) the compositional dependence of T_c and T_M of $LaSe_x$ and LaS_x, and (3) the pressure dependence of T_c for various La:S ratios.

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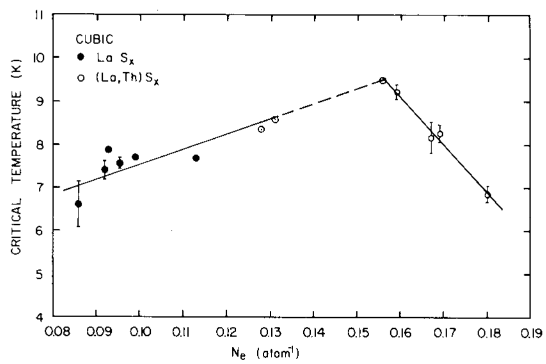

FIGURE 1. T_c as a function of electron concentration.

II. ALLOYING STUDIES

Alloys of 2 or 3 at.% Ca, Y, Ce or Th in La were reacted with S to give nominal R_3S_4. The preliminary results indicated that Ca lowers T_c, Y and Ce have little or no effect on T_c and Th raises T_c. On the basis of these data a more extensive study was made of $(La,Th)S_x$, with $x \simeq 1.33$ for most alloys, but a few samples contained more sulfur up to $x = 1.40$. It was found that: (1) T_c is raised to 9.5 K by the substitution of 3 at.% Th for La, (2) at higher Th concentrations, T_c falls off, and (3) the bcc → tetragonal transformation is suppressed. The variation of T_c for the cubic phase alloys in the $(La,Th)S_x$ system is shown in Fig. 1 as a function of electron concentration. The shape of the curves is thought to be due to two competing effects. The increase in T_c is due to the availability of a larger number of conduction electrons as either Th is substituted for La, or as the S:R ratio decreases. The decrease in T_c is due to the replacement of La by Th which disrupts the superconducting chains of La atoms. The latter effect probably becomes more pronounced as more and more Th atoms are substituted, i.e. it has a non-linear concentration dependence.

III. VARIATION OF T_c AND T_M FOR LaS_x AND $LaSe_x$ ALLOYS ($x < 1.37$)

For the stable cubic LaS_x (Ikeda, et al., 1980 and 1982) and $LaSe_x$ (Holtzberg et al., 1968) T_c is found to increase as the number of conduction electrons increases (i.e. as x decreases). For the alloys which transform to the tetragonal phase at low temperatures our recent studies show that T_c decreases with decreasing x (or increasing electron concentration), see Fig. 2. The data show that in the thermodynamically stable phases (bcc and tetragonal at ≃10 K) the superconducting transition temperature tends toward a maximum as the lattice instability increases, i.e. T_c is a maximum at x_c.

The variation of T_M in LaS_x, $(La_{0.97}Th_{0.03})S_x$ and $LaSe_x$ as a function of electron concentration is shown in Fig. 3. For the binary alloys T_M is found to increase as the number of conduction electrons increases (or as the S:R ratio decreases). But for both Th containing alloys the cubic phase is found to be stable down to 4 K. These results, that N_e at T_M = 0 K for LaS_x and $LaSe_x$ are different and the absence of a transformation in $(La,Th)S_x$, are interesting since they rule out the suggestion that this transformation occurs at a "magic" electron concentration. However, electron concentration may play a minor role, along with the Jahn-Teller effect (Westerhold, et al., 1980) and lattice strains in determining whether or not the bcc phase will transform to the tetragonal form.

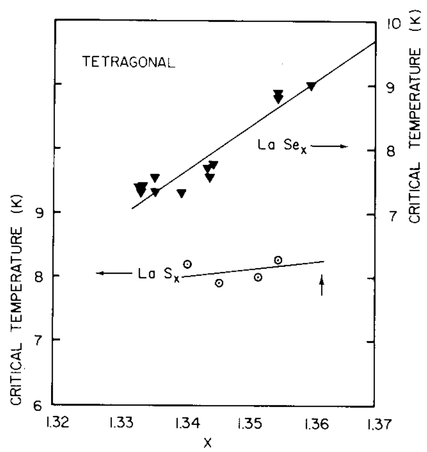

FIGURE 2. T_c vs. S:R ratio, x, for the tetragonal LaS_x and $LaSe_x$ alloys. The arrow for LaS_x indicates the critical concentration at which T_M = 0 K. For $LaSe_x$ $x_c \simeq 1.375$.

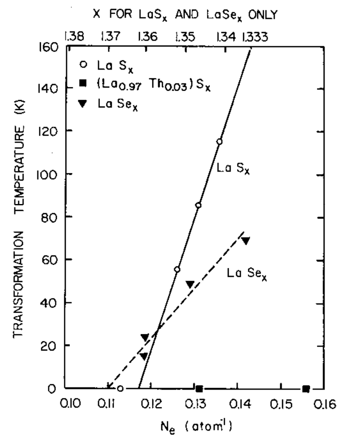

FIGURE 3. The dependence of the bcc - tetragonal transformation temperature on the electron concentration.

IV. HEAT CAPACITY AT HIGH MAGNETIC FIELDS

High magnetic fields (up to 10 T) were used to quench superconductivity, so that reliable heat capacity data in the normal state material could be taken to as low a temperature as possible. Several important superconducting properties [e.g. $H_{c2}(0)$, κ_0, ξ_0 and $\lambda_L(0)$] were also derived from these data. The properties of several compositions were reported by Ikeda et al. (1982) for the LaS_x alloys. Initial results on a $LaSe_x$ alloy (tetragonal phase) indicate T_c, γ (the electronic specific heat constant) and $H_{c2}(0)$ are larger than the corresponding values for the LaS_x alloy with the same chalcogenide to metal ratio, see Table 1. The data suggest that the $LaSe_x$ alloys should have better superconducting properties than the LaS_x alloys for the same x value. However, this needs to be verified experimentally.

TABLE I. Some normal and superconducting state properties of the tetragonal $LaX_{1.355}$ alloys.

Sample	T_c (K)	γ $\frac{mJ}{g\text{-}at.K^2}$	Θ_D (K)	$H_{c2}(0)$ (T)	ρ_r ($\mu\Omega$-cm)
$LaS_{1.355}$	8.29	2.98	220	11.67	156
$LaSe_{1.355}$	8.61	5.56	185	13.2	117

V. HYDROSTATIC PRESSURE STUDIES

The pressure dependence of T_c up to 22 kbar for four LaS_x samples has been measured by a low frequency inductance technique in a standard Be-Cu clamp for maintaining pressure at low temperatures (Jayaraman, et al., 1967), see Fig. 4. A non-linearity in the pressure dependence of T_c is evident in the three

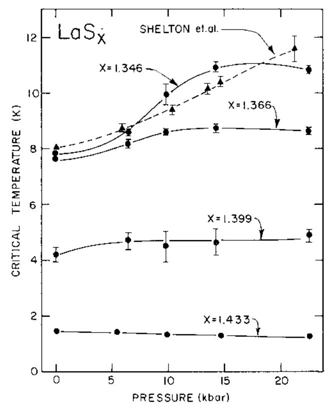

FIGURE 4. T_c vs. pressure for LaS_x. Error bars indicate transition widths. The dashed line shows the previous results on "La_3S_4" whose exact composition is unknown (Shelton, et al. 1975).

lower x value samples with two samples (x = 1.346 and 1.366) showing distinct maxima. Together with the results reported previously (Eiling, et al., 1981) the maximum in T_c is seen to move to lower pressures with increasing x until it is entirely absent in $LaS_{1.433}$. The pressure dependence of T_c for samples which retain the bcc phase varies with composition, but is greatly reduced when compared to $T_c(p)$ for samples in the tetragonal phase. Our x = 1.346 sample, as well as those transforming samples previously studied (Shelton et al, 1975 and Eiling et al. 1982) shows an exceptionally large increase in T_c leading to a maximum in $T_c(p)$ at higher pressures. This rapid increase in T_c with pressure is consistent with the known suppression of the crystallographic transformation by pressure (Shelton, et al., 1975) since the T_c of the bcc phase at these S:La ratios is expected to be significantly higher ($\Delta T_c \sim 1.6$ K for $LaS_{1.346}$ and is even greater for smaller x values) than that of the tetragonal phase with the same S:La ratio (see Fig. 11 of Ikeda et al., 1982). This pressure-induced suppression of the crystallographic transformation would account for the large increase in T_c relative to the pressure dependence of T_c of the non-transforming samples.

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